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THE UNIVERSITY OF ALBERTA

Potential Release of Phosphorus From Shallow Sediments to Lakewater

by

Jacqueline Francoise Helene Shaw

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF ZOOLOGY

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ABSTRACT

The significance of shallow sediments as a source of phosphorus (P) for north-temperate lakes in central Alberta was investigated by: (1) examining relationships between characteristics of porewater and particulate sediments and total P (TP) concentrations in the trophogenic zone (TZP) of nine eutrophic lakes, and (2) calculating trophogenic TP budgets for 16 eutrophic lakes. No direct correlations between porewater or particulate sediment parameters and TZP were found. However, average lake values of a mobile porewater P component that was determined with principal component analysis were positively correlated with TZP. This relationship indicates that mobile P in porewater of shallow sediments may affect TZP. Average lake values of a principal component which consisted primarily of particulate P fractions were not correlated with TZP.

Summer trophogenic TP budgets for 16 lakes were calculated based on TP inputs to the lakes from atmospheric deposition, runoff from the watershed, and TP outputs from the lakes by stream outflow, and sedimentation. On average, substantially more TP was measured in trophogenic lakewater than could be accounted for by the TP budgets; this discrepancy (TP_d) indicated that there was a missing source of P to the trophogenic zone. TP_d was correlated with the proportion of shallow sediments to lake surface area which suggests that P release from shallow sediments contributes P to the trophogenic zone. At five lakes, release of P from shallow sediments by molecular diffusion and groundwater accounted for 13 and 5% of TP_d, respectively. In addition, other mechanisms such as bioturbation and mixing in sediments may

transport P from shallow sediments into lakewater.

Shallow sediments are usually ignored as a P source to lakes. However, results from this study indicate that P release from shallow sediments occurs. For some lakes, the estimated rates of P release from shallow sediments to lakewater were higher than external sources of P. Thus, P release from shallow sediments should not be ignored during investigations of P cycling in lakes.

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1. GENERAL INTRODUCTION

Phosphorus (P) is the nutrient limiting biological productivity in most lakes (Hutchinson 1957; Vollenweider 1968). In previous studies, concentrations of P in surface water were correlated to algal standing crop, primary productivity, benthic biomass and fish yield (e.g., Sakamoto 1966; Dillon and Rigler 1974; Smith 1979; Hanson and Leggett 1982). Experimental additions of P to lakes resulted in increased algal biomass, and fish growth and production (Schindler et al. 1973; Stockner 1981). Numerous loading models were developed to determine the effect of external P sources on P concentrations or algal biomass in the trophogenic zone of lakes (e.g., Vollenweider 1968; Dillon and Rigler 1975); internal sources of P are ignored in these models. However, P budgets constructed for the epilimnion or the entire water volume of relatively small, stratified lakes revealed that outputs and external inputs of P could not explain the amount of P present in either the epilimnion or the entire lake (Hutchinson 1941; Lie 1977; Caraco et al. 1988). Thus, internal sources of P (i.e., P released from bottom sediments) may influence P concentrations in the trophogenic zone of relatively small lakes.

Internal P sources: hypolimnetic versus epilimnetic sediments

Release of P from hypolimnetic sediments into anaerobic lakewater can be substantial (e.g., Mortimer 1941). P, released from hypolimnetic sediments, accumulates in the hypolimnion; it enters the epilimnion only when the P gradient across the thermocline is large and when the thermocline is depressed (Imboden and Emerson 1978; Kortmann et al.

1982; Stauffer and Armstrong 1984). In deep, well-stratified lakes, transport of P from the hypolimnion only influences epilimnetic P concentrations during turnover events (spring or fall) or during late summer when P gradients across the thermocline have developed (e.g., Schindler et al. 1980; Kortmann et al. 1982). Thus, internal P release from shallow (epilimnetic) sediments may balance P missing in epilimnetic budgets during the summer (Lie 1977; Caraco et al. 1988).

Phosphorus released from shallow sediments enters aerobic epilimnetic water, where it is available to algae. Thus, the impact of P released from sediments into the aerobic epilimnion is more immediate than that released into the anaerobic hypolimnion (i.e., mixing events are not required). Although sediment P release rates into aerobic water are generally lower than those into anaerobic water (at 18 ^{o}C or less; Kamp-Nielsen 1975), sediment P release rates into aerobic water have been reported as high as 83 $mg.m^{-2}.d^{-1}$, and averaged 5 $mg.m^{-2}.d^{-1}$ (Table 1.1). Conclusions from ^{32}P additions to lakes also indicated potential exchange of P between epilimnetic sediments and surface waters (e.g., Hutchinson and Bowen 1950; Hayes et al. 1952; Rigler 1956). In addition, there is indirect evidence that P release from shallow sediments may occur: (1) phosphorus turnover rates were related to the ratio of water volume to mud surface of mixed (i.e., not thermally stratified) lakes (Hayes et al. 1952), and (2) primary production was related to the ratio of sediment area to water volume in the epilimnion of stratified lakes (Fee 1979).

P sources for release from sediments

Release of P from sediments to lakewater occurs through the (mobile) porewater P fraction (Syers et al. 1973; Bostrom et al. 1982); P release rates increased with greater gradients across the sediment-water interface (Ulen 1978). Phosphorus in porewater is the smallest P fraction (by mass) in sediments. Thus, an understanding of the exchange between P in particulate sediments and in porewater is important to determine the potential for sustained P release from porewater. Iron-bound P fractions in particulate sediments (determined by several different chemical extraction techniques) are correlated with desorption of P, algal growth, and P release from sediments (Williams et al. 1980; Hosomi et al. 1981; Young and DePinto 1982; Messer et al. 1984; Drake and Heany 1987; Nurnberg 1988). Organic-bound P can also be involved in exchange reactions; it is solubilized by bacterial decomposition (e.g., Sinke and Cappenberg 1988). Organic-bound P is analyzed as the difference between inorganic and total P. During the inorganic P extraction procedures, NaOH and HCl are used. However, in addition to inorganic P forms, NaOH and HCl solubilize labile organic-bound P. The most labile forms of organic P are analyzed as iron-bound P (e.g., Bostrom et al. 1982; Psenner et al. 1984). Thus, iron-bound P fractions most likely exchange P with porewater.

P exchange between particulate sediments and porewater

Sorption capacity of the mud and redox condition influence P exchange between particulate fractions and porewater. Exchange of P between sediments and water is also influenced by pH; calcium precipitates P at high pH and iron sorbs P at low pH (e.g., Stumm and

Leckie 1970; Lijklema 1977). Adsorption of P to particulate sediments is stronger at low pH and under aerobic conditions than at high pH and under anaerobic conditions (Golachowska 1971; Lijklema 1977; Ku et al. 1978; Golterman 1988). Consequently, P release from sediments to water was less at low pH (4 to 8) and under aerobic conditions than at high pH (9 to 11) and under anaerobic conditions (Ohle 1937; Andersen 1975; Rippey 1977; Ulen 1978; Holdren and Armstrong 1980; Jacoby et al. 1982; Drake and Heany 1987; Fabre 1988). Thus, sorption capacity, redox condition and pH in sediments can affect porewater P concentrations, which in turn can influence P release from porewater to overlying lakewater.

P release from porewater to lakewater

Phosphorus is transported from sediment porewater to overlying lakewater by molecular diffusion, bioturbation, physical mixing (i.e., without resuspension of particulate sediments) and groundwater flow. Resuspension and macrophytes may also influence P release from sediments to overlying water. The effect of resuspended particulate sediments on P concentrations in the trophogenic zone is not clear; resuspension increased or did not change total P concentrations in lakewater (Serruya et al. 1978; Peters and Cattaneo 1984). Macrophyte roots meet most of their P demand (>70%) from particulate sediments (Carignan and Kalff 1980). Although healthy macrophyte shoots release little P into lakewater, P may be released into lakewater upon decay of macrophyte shoots (DeMarte and Hartman 1974; Peverly and Brittain 1978; Carpenter 1980; Barko and Smart 1980,1981; Carignan and Kalff 1982). Release of P due to decay of macrophyte shoots is small during the summer.

Consequently, I ignored P release from shallow sediments to lakewater by resuspension and via macrophytes. Instead, I focussed on P transport from porewater directly to lakewater.

Transport of P from porewater to lakewater by molecular diffusion and bioturbation is enhanced at higher temperatures (Banoub 1975; Kamp-Nielsen 1975; Lee et al. 1977; Gallepp 1979; Holdren and Armstrong 1980; Gardner et al. 1981; Boers and Van Hese 1988). Sediment P release by bioturbation is greater than by molecular diffusion (Gallepp 1979; Graneli 1979; Van Eck and Smits 1986). In addition, bioturbation affects release rates of P more than changes in temperature, mixing, redox condition and sediment type (Holdren and Armstrong 1980). Physical mixing may not only increase P transport across the sediment-water interface (Holdren and Armstrong 1980); since resistance to mixing is small in isothermal epilimnetic waters, physical mixing of lakewater also distributes sediment-released P just above the sediment-water interface into the entire epilimnion. Thus, a steep P gradient across the sediment-water interface is maintained, which also maintains P release by molecular diffusion and bioturbation. In addition, groundwater flow into overlying lakewater contributes P to surface waters and enhances release of P in core incubations in the laboratory (Fillos 1977; Brock et al. 1982; Peters and Van Liere 1985).

Framework of thesis

The goal of this research was to assess the potential importance of P release from shallow sediments (located in the epilimnion or trophogenic zone) to lakes. Most of this work was carried out at Narrow Lake, Alberta, a stratified, meso-eutrophic lake. To determine how

results from Narrow Lake compared with other eutrophic lakes, I sampled eight other Alberta lakes which varied in depth (and thus ranged from thermally stratified to mixed) and trophic status (meso-eutrophic to hypereutrophic). To investigate the potential importance of P release from shallow sediments, the following studies were carried out:

To determine whether P release from the mobile porewater fraction was possible, P gradients across the sediment-water interface were measured at several sites during two summers at Narrow Lake. With these gradients, diffusion of P from porewater to lakewater by diffusion was calculated (Chapter 2).

To determine whether P release from porewater could be sustained by P exchange from particulate sediments, particulate P fractions and iron, P and pH in porewater were analyzed in nine lakes. Particulate P fractions, porewater parameters and porosity were correlated to determine if simple relationships suggested that (1) a single particulate fraction likely exchanged P with porewater, and (2) a single variable could inhibit P exchange between particulate sediments and porewater (Chapter 3).

Chapters 2 and 3 also describe in detail the methods used to collect and analyze porewater and particulate sediments. The porewater and particulate sediment data are described and compared to other studies. The following chapters (4-6) analyze these data in more detail to determine the potential of P release from shallow sediments.

Release of P from shallow sediments to surface waters more likely affects P concentrations in lakewater during summer than P transport from the hypolimnion. To determine whether P release from shallow sediments could affect P concentrations in the trophogenic zone,

(1) particulate sediments, porewater and lakewater just above the sediment-water interface were collected at several sites in seven lakes, (2) a principal component analysis was performed to condense the number of parameters, and (3) the principal components were correlated with P concentrations in the trophogenic zone (Chapter 4).

To determine the potential importance of internal P release to lakes during summer, short-term budgets were calculated (excluding internal P sources) for the trophogenic zone of 16 deep, stratified lakes. The potential P transport from the hypolimnion to the epilimnion of eight of these lakes was evaluated based on P gradients across the thermocline. In addition, potential release of P from shallow sediments into the epilimnion was calculated from P gradients across the sediment-water interface at several shallow sites in five of the 16 lakes. Potential P release from internal sources (i.e., hypolimnion or shallow sediments) was compared to discrepancies in short-term P budgets (Chapter 5).

Because P may be transported into lakewater by groundwater flow through sediments, transport of P by molecular diffusion may underestimate _in situ_ fluxes. Therefore, P transport by groundwater was measured at six lakes (Chapter 6).

Evidence of P release from shallow sediments to surface waters is difficult to obtain: (1) laboratory experiments cannot simulate P release from sediments under _in situ_ lake conditions (with mixing, groundwater flow, sedimentation and bioturbation), and (2) P cycling in lakes is too complex to isolate the impact of P release from shallow sediments on lakewater, from other processes (external P sources, many P compartments and sinks). Therefore, this study integrates several

approaches (as outlined above) to indirectly (but convincingly) determine the potential of P release from shallow sediments of several lakes.

1.1 REFERENCES

Andersen, J. M. 1975. Influence of pH on release of phosphorus from lake sediments. Arch. Hydrobiol. 76:411-419.

Banoub, M. W. 1975. Experimental studies on material transactions between mud and water of the Gnadensee (Bodensee). Verh. Internat. Verein. Limnol. 19:1263-1271.

Barko, J. W., and R. M. Smart. 1980. Mobilization of sediment phosphorus by submersed freshwater macrophytes. Freshwater Biol. 10:229-238.

Barko, J. W., and R. M. Smart. 1981. Sediment-based nutrition of submersed macrophytes. Aquat. Bot. 10:339-352.

Boers, P. C. M., and O. Van Hese. 1988. Phosphorus release from the peaty sediments of the Loosdrecht lakes (the Netherlands). Wat. Res. 22:355-363.

Bostrom, B., M. Jansson, and C. Forsberg. 1982. Phosphorus release from lake sediments. Arch. Hydrobiol. 18:5-59.

Brock, T. D., D. R. Lee, D. Jones, and D. Winek. 1982. Groundwater seepage as a nutrient source to a drainage lake; Lake Mendota, Wisconsin. Wat. Res. 16:1255-1263.

Caraco, N. F., J. J. Cole, G. E. Likens, M. D. Mattson, and S. Nolan. 1988. A very imbalanced nutrient budget for Mirror Lake, New Hampshire, U.S.A. Verh. Internat. Verein. Limnol. 23:170-175.

Carignan, R., and J. Kalff. 1980. Phosphorus sources for aquatic weeds: water or sediments. Science 207:987-989.

Carignan, R., and J. Kalff. 1982. Phosphorus release by submerged macrophytes: significance to epiphyton and phytoplankton. Limnol. Oceanogr. 27:419-427.

Carpenter, S. R. 1980. Enrichment of Lake Wingra, Wisconsin, by submersed macrophyte decay. Ecology 61:1145-1155.

Conley, D. J., M. A. Quigley, and C. L. Schelske. 1988. Silica and phosphorus flux from sediments: importance of internal recycling in Lake Michigan. Can. J. Fish. Aquat. Sci. 45:1030-1035.

DeMarte, J. A., and R. T. Hartman. 1974. Studies on absorption of ^{32}P, ^{59}Fe, and ^{45}Ca by water-milfoil (Myriophyllium exalbens Fernald). Ecology 55:188-194.

Dillon, P. J., and F. H. Rigler. 1974. The phosphorus-chlorophyll relationship in lakes. Limnol. Oceanogr. 19:767-773.

Dillon, P. J., and F. H. Rigler. 1975. A simple method for predicting the capacity of a lake for development based on lake trophic status. J. Fish. Res. Board Can. 32:1519-1531.

Drake, J. C., and S. I. Heany. 1987. Occurrence of phosphorus and its potential remobilization in the littoral sediments of a productive English lake. Freshwater Biol. 17:513-523.

Fabre, A. 1988. Experimental studies on some factors influencing phosphorus solubilization in connection with the drawdown of a reservoir. Hydrobiologia 159:153-158.

Fee, E. J. 1979. A relation between lake morphometry and primary productivity and its use in interpreting whole-lake eutrophication experiments. Limnol. Oceanogr. 24:401-416.

Fillos, J. 1977. Effect of sediments on the quality of the overlying water. p. 266-271. In H. L. Golterman (ed.). Interactions between sediments and freshwater (Proc. S.I.L.-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands.

Fillos, J., and W. R. Swanson. 1975. The release rate of nutrients from

river and lake sediments. J. Water Poll. Control Fed. 47:1032-1042.

Gallepp, G. W. 1979. Chiromid influence on phosphorus release in sediment-water microcosms. Ecology 60:547-556.

Gallepp, G. W., J. F. Kitchell, and S. M. Bartell. 1978. Phosphorus release from lake sediments as affected by chironomids. Verh. Internat. Verein. Limnol. 20:458-465.

Gardner, W. S., T. F. Nalepa, M. A. Quigley, and J. M. Malczyk. 1981. Release of phosphorus by certain benthic invertebrates. Can. J. Fish. Aquat. Sci. 38:978-981.

Golachowski, J. B. 1971. The pathways of phosphorus in lake water. Pol. Arch. Hydrobiol. 18:325-345.

Golterman, H. L. 1988. The calcium- and iron bound phosphate phase diagram. Hydrobiologia 159:149-151.

Graneli, W. 1979. The influence of Chironomus plumosus larvae on the exchange of dissolved substances between sediment and water. Hydrobiologia 66:149-159.

Hanson, J. M., and W. C. Leggett. 1982. Empirical prediction of fish biomass and yield. Can. J. Fish. Aquat. Sci. 39:257-263.

Hayes, F. R., J. A. McCarter, M. L. Cameron, and D. A. Livingstone. 1952. On the kinetics of phosphorus exchange in lakes. J. Ecol. 40:202-216.

Holdren, G. C., and D. E. Armstrong. 1980. Factors affecting phosphorus release from intact lake sediment cores. Environ. Sci. Technol. 14:79-87.

Hosomi, M., M. Okada, and R. Sudo. 1981. Release of phosphorus from sediments. Verh. Internat. Verein. Limnol. 21:628-633.

Hutchinson, G. E. 1941. Limnological studies in Connecticut. IV. The

mechanism of intermediary metabolism in stratified lakes. Ecol. Monographs 11:21-60.

Hutchinson, G. E. 1957. A Treatise on Limnology. Vol. I Geography, physics and chemistry. J. Wiley & Sons, Inc., New York. 1015p.

Hutchinson, G. E., and V. T. Bowen. 1950. Limnological studies in Connecticut. IX. A quantitative radiochemical study of the phosphorus cycle in Linsley Pond. Ecology 31:194-203.

Imboden, D. M., and S. Emerson. 1978. Natural radon and phosphorus as limnologic tracers: horizontal and vertical eddy diffusion in Greifensee. Limnol. Oceanogr. 23:77-90.

Jacoby, J. M., D. D. Lynch, E. B. Welch, and M. A. Parkins. 1982. Internal phosphorus loading in a shallow eutrophic lake. Wat. Res. 16:911-919.

Kamp-Nielsen, L. 1974. Mud water exchange of phosphate and other ions in undisturbed sediment cores and factors affecting the exchange rates. Arch. Hydrobiol. 73:218-237.

Kamp-Nielsen, L. 1975. A kinetic approach to the aerobic sediment-water exchange of phosphorus in Lake Esrom. Ecol. Model. 1:153-160.

Kortmann, R. W., D. D. Henry, A. Kuether, and S. Kaufman. 1982. Epilimnetic nutrient loading by metalimnetic erosion and resultant algal responses in Lake Waramaug, Connecticut. Hydrobiologia 92:501-510.

Ku, W. C., F. A. DiGiano, and T. H. Feng. 1978. Factors affecting phosphate adsorption equilibria in lake sediments. Wat. Res. 12:1069-1074.

Lee, G. F., W. C. Sonzogni, and R. D. Spear. 1977. Significance of oxic vs. anoxic conditions for Lake Mendota sediment phosphorus release.

p. 294-306. In H. L. Golterman (ed.). Interactions between sediments and freshwater (Proc. S.I.L.-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands.

Lennox, L. J. 1984. Lough Ennell: laboratory studies on sediment phosphorus release under varying mixing, aerobic and anaerobic conditions. Freshwater Biol. 14:183-187.

Lie, G. B. 1977. Aspects of the ecology and physiology of freshwater macrophytes: phosphorus cycling by freshwater macrophytes, the case of Shagawa Lake. PhD. thesis, University of Minnesota-Minneapolis, Minneapolis, MN. 63p.

Lijklema, L. 1977. The role of iron in the exchange of phosphate between water and sediments. p. 313-317. In H. L. Golterman (ed.). Interactions between sediments and freshwater (Proc. S.I.L.-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands.

Mawson, S. J., H. L. Gibbons, W. H. Funk, and K. E. Hartz. 1983. Phosphorus flux rates in lake sediments. J. Water Poll. Control. Fed. 55:1105-1110.

Messer, J. J., J. M. Ihnat, and D. L. Wegner. 1984. Phosphorus release from the sediments of Flaming Gorge Reservoir, Wyoming, U.S.A. Verh. Internat. Verein. Limnol. 22:1457-1464.

Mortimer, C. H. 1941. The exchange of dissolved substances between mud and water in lakes. J. Ecol. 29:280-329.

Nurnberg, G. K. 1988. Prediction of phosphorus release rates from total and reductant-soluble phosphorus in anoxic lake sediments. Can. J. Fish. Aquat. Sci. 45:453-462.

Ohle, W. 1937. Kolloidgele als Nahrstoffregulatoren der Gewasser. Naturwissenschaften 25:471-474.

Peters, J., and L. Van Liere. 1985. Dredging and groundwater-movement, effects on phosphorus release from sediments. Verh. Internat. Verein. Limnol. 22:3340-3344.

Peters, R. H., and A. Cattaneo. 1984. The effects of turbulence on phosphorus supply in a shallow bay of Lake Memphremagog. Verh. Internat. Verein. Limnol. 22:185-189.

Peverly, J. H., and J. Brittain. 1978. Effects of milfoil (Myriophyllum spicatum L.) on phosphorus movement between sediment and water. J. Great Lakes Res. 4:62-68.

Psenner, R., R. Pucsko, and M. Sager. 1984. Die Fraktionierung organischer und anorganischer Phosphorverbindungen von Sedimenten. Arch. Hydrobiol. Suppl. 70:111-155.

Quigley, M. A., and J. A. Robbins. 1986. Phosphorus release processes in nearshore southern Lake Michigan. Can. J. Fish. Aquat. Sci. 43:1201-1207.

Rigler, F. H. 1956. A tracer study of the phosphrus cycle in lake water. Ecology 37:550-562.

Rippey, B. 1977. The behaviour of phosphorus and silicon in undisturbed cores of Lough Neagh sediments. p. 345-353. In H. L. Golterman (ed.). Interactions between sediments and freshwater (Proc. S.I.L.-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands.

Ryding, S. O., and C. Forsberg. 1977. Sediments as a nutrient source in shallow polluted lakes. p. 227-234. In H. L. Golterman (ed.). Interactions between sediments and freshwater (Proc. S.I.L.-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands.

Sakamoto, M. 1966. Primary production by phytoplankton community in some Japanese lakes and its dependence on lake depth. Arch. Hydrobiol.

62:1-28.

Schindler, D. W., R. Hesslein, and G. Kipphut. 1977. Interactions between sediments and overlying waters in natural oligotrophic and experimentally-eutrophied Precambrian Shield lakes. p. 235-243. In H. L. Golterman (ed.). Interactions between sediments and freshwater (Proc. S.I.L.-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands.

Schindler, D. W., H. Kling, R. V. Schmidt, J. Prokopowitz, V. E. Frost, R. A. Reid, and M. Capel. 1973. Eutrophication of Lake 227 by addition of phosphate and nitrate: the second, third, and fourth years of enrichment, 1970, 1971, and 1972. J. Fish. Res. Board Can. 30:1415-1440.

Schindler, D. W., T. Ruszczynski, and E. J. Fee. 1980. Hypolimnion injection of nutrient effluents as a method for reducing eutrophication. Can. J. Fish. Aquat. Sci. 37:320-327.

Serruya, C., S. Serruya, and U. Pollingher. 1978. Wind, phosphorus release and division rate of Peridinium in Lake Kinneret. Verh. Internat. Verein. Limnol. 20:1096-1102.

Sinke, A. J. C., and T. E. Cappenberg. 1988. Influence of bacterial processes on the phosphorus release from sediments in the eutrophic Loosdrecht Lakes, The Netherlands. Arch. Hydrobiol. Beih. 30:5-13.

Smith, V. H. 1979. Nutrient dependence of primary productivity in lakes. Limnol. Oceanogr. 24:1051-1064.

Stauffer, R. E., and D. E. Armstrong. 1984. Lake mixing and its relationship to epilimnetic phosphorus in Shagawa Lake, Minnesota. Can. J. Fish. Aquat. Sci. 41:57-69.

Stockner, J. G. 1981. Whole-lake fertilization for the enhancement of

sockeye salmon (Oncorhynchus nerka) in British Columbia, Canada. Verh. Internat. Verein. Limnol. 21:293-299.

Stumm, W., and J. O. Leckie. 1970. Phosphate exchange with sediments: its role in the productivity of surface waters. Proc. Int. Water Poll. Res. Conf. 5th: San Francisco and Hawaii 3: Art. 26. 16p.

Syers, J. K., R. F. Harris, and D. E. Armstrong. 1973. Phosphate chemistry in lake sediments. J. Environ. Qual. 2:1-14.

Twinch, A. J., and R. H. Peters. 1984. Phosphate exchange between littoral sediments and overlying water in an oligotrophic north-temperate lake. Can J. Fish. Aquat. Sci. 41:1609-1617.

Ulen, B. 1978. Seston and sediment in Lake Norrviken. III. Nutrient release from sediment. Schweiz. Z. Hydrol. 40:287-305.

Van Eck, G. Th. M., and J. G. C. Smits. 1986. Calculation of nutrient fluxes across the sediment-water interface in shallow lakes. p. 289-301. In P. G. Sly (ed.). Sediments and Water Interactions. Proc. 3rd. Int. Symp. on Interactions between Sediments and Water (Geneva, Switzerland, Aug. 27-31, 1984). Springer-Verlag, New York, NY. 521p.

Vollenweider, R. A. 1968. Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorus as factors in eutrophication. OECD Rep. DAS/CSI/68-27. Organization for Economic Co-operation and Development, Directorate for Scientific Affairs, Paris.

Williams, J. D. H., H. Shear, and R. L. Thomas. 1980. Availability to Scenedesmus quadricauda of different forms of phosphorus in sedimentary materials from the Great Lakes. Limnol. Oceanogr. 25:1-11.

Young, T. C., and J. V. DePinto. 1982. Algal availability of particulate phosphorus from diffuse and point sources in the lower Great Lakes Basin. Hydrobiologia 91:111-119.

Table 1.1 Sediment release rates of phosphorus into aerobic lakewater from bottom sediments during laboratory core incubations.

Reference	Release rate ($mg.m^{-2}.d^{-1}$)
Kamp-Nielsen 1974	-2 to 0.6
Fillos and Swanson 1975	1.2 to 9.6
Rippey 1977	10.4
Ryding and Forsberg 1977	0.3 to 2
Schindler et al. 1977	0
Gallepp et al. 1978	4 to 6
Ulen 1978	1.7 to 6.7
Gallepp 1979	0 to 4.1
Graneli 1979	0.3 to 11.4
Holdren and Armstrong 1980	-1.9 to 83
Jacoby et al. 1982	5.6
Mawson et al. 1983	0.1
Lennox 1984	1
Messer et al. 1984	0.2 to 2.1
Twinch and Peters 1984	2
Quigley and Robbins 1986	0.2 to 0.6
Drake and Heany 1987	1 to 2
Conley et al. 1988	0.05
Sinke and Cappenberg 1988	3.5 to 16.5

2. TEMPORAL AND SPATIAL PATTERNS OF POREWATER PHOSPHORUS IN SHALLOW SEDIMENTS, AND ITS POTENTIAL TRANSPORT INTO NARROW LAKE, ALBERTA[1]

2.1 ABSTRACT

During 1985 and 1986, summer and spatial patterns of porewater soluble reactive phosphorus (SRP) from sediments $\leq$ 15-m depth were examined at Narrow Lake, a deep, meso-eutrophic lake in Alberta. At three sites (different in depth and macrophyte colonization), trends in porewater SRP concentrations ([SRP]) in the top 5 cm of the sediment varied from May to August, possibly due to root uptake of SRP by macrophytes. At a depth of 5 m, mean (in the top 5 cm of the sediment) and variance of porewater [SRP] at one site ($< 0.15\ m^2$) were the same as over the entire lake. Excluding data from macrophyte sites, porewater [SRP] were positively related to depth of the water column ($P < 0.0001$). Molecular diffusion of SRP into the trophogenic zone was calculated from sediments with and without macrophytes. During summer, molecular diffusion from shallow sediments to the trophogenic zone was 0.05 $mg.m^{-2}.d^{-1}$, or 29% of atmospheric deposition of P (the major external source of P to the lake). At lakes with similar morphometry and trophic status to Narrow Lake, a sampling strategy is discussed to enable the calculation of whole-lake P transport from shallow sediments to the trophogenic zone.

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2.2 INTRODUCTION

Phosphorus (P) is the major limiting nutrient for algal productivity in many freshwater lakes (Schindler 1977). P can be released from lake sediments into anaerobic lakewater (e.g., Einsele 1936, 1938; Ohle 1937; Einsele and Vetter 1938; Mortimer 1941, 1942; Nurnberg 1984; Riley and Prepas 1984), or into aerobic lakewater at high temperature and neutral to basic pH (Andersen 1975; Banoub 1975; Kamp-Nielsen 1975; Lee et al. 1977; Rippey 1977; Ku et al. 1978; Ulen 1978; Holdren and Armstrong 1980). In thermally stratified lakes, sediment P release during summer into anaerobic (hypolimnetic) lakewater is easier to quantify than release into aerobic (trophogenic) lakewater. Phosphorus, released into an anaerobic hypolimnion, accumulates below the thermocline. Transport of P from the hypolimnion into the epilimnion occurs only when the thermocline erodes (Quay et al. 1980; Schindler et al. 1980; Kortmann et al. 1982; Stauffer and Armstrong 1984) or when the P gradient across the thermocline is large (Imboden and Emerson 1978). Thus, little of the P released from hypolimnetic sediments is available to algae during summer stratification. This release can be estimated from changes in hypolimnetic P mass over time.

In contrast, relatively little is known about sediment P release from shallow sediments (i.e., those sediments located in the trophogenic zone) into aerobic lakewater. Since the trophogenic zone usually contains a much larger volume of water than the hypolimnion, P released from shallow sediments is diluted more than P released from hypolimnetic sediments. P released from these shallow sediments does not remain in solution in the trophogenic zone of P-limited lakes; it is taken up by

algae, cycled through other trophic levels, and removed from the trophogenic zone by sedimentation. An increase of P in the trophogenic zone may also be caused by allochtonous P inputs. Thus, an increase in trophogenic P due to release from shallow sediments is difficult to quantify.

Release of P from shallow sediments into aerobic lakewater has been estimated either from P budgets or from core incubations and porewater samples. Estimates of sediment P release calculated as the residual in a P budget include the compounded error of other parameters in the budget. Incubations of cores in the laboratory oversimplify sediment-lake systems by failing to include important factors such as bioturbation, mixing and groundwater flow (e.g., Gallepp 1979; Holdren and Armstrong 1980; Van Liere and Mur 1982). In situ estimates of P release have been based on gradients of porewater P, which is the most mobile form of P in the sediment (Syers et al. 1973; Bostrom et al. 1982). These rates are likely underestimates of P release because: (1) P gradients near the sediment-water interface may be steeper than between the top 3 cm of the sediment and the overlying water, and (2) P transport by bioturbation and mixing may be greater than by molecular diffusion. In addition, these estimates of sediment P release are based on a single collection of porewater (Bannerman et al. 1974; Quigley and Robbins 1986). Porewater P concentrations can vary over spring and the open water season, within one depth, with lake depth, and with macrophyte colonization (Bannerman et al. 1974; Holdren et al. 1977; Carignan 1984a, 1985; Carignan and Nriagu 1985; Kawai et al. 1985; Smith and Adams 1986; Drake and Heany 1987). However, these studies provided only limited information on seasonal and spatial patterns of porewater P

in lakes during summer. Thus, it is difficult to calculate a "whole-lake" sediment P release rate into aerobic lakewater.

During 1985 and 1986, porewater and lakewater samples near the sediment-water interface were collected at Narrow Lake, a deep meso-eutrophic lake in Alberta. The variability of porewater P concentrations in shallow sediments was examined with depth in the sediment, at sites with and without macrophytes, from May to August, within a single depth over the entire lake, and between depths. These results were used to calculate potential P release from shallow sediments into the trophogenic zone during the summer, and to outline strategies for sampling porewater P at other lakes.

2.3 MATERIAL AND METHODS

Study area

Narrow Lake is located in central Alberta (54°35' N, 113°37' W) in the mixed-wood section of the boreal forest (Strong and Leggat 1981). Drift, primarily glacial till interbedded with alluvial deposits, surrounds the lake. Sedimentary bedrock lies 5 to 10 m underneath the deepest part of the lake (Green 1972; Kjearsgaard 1972). Narrow Lake is a small, relatively deep, meso-eutrophic lake (surface area 1.1 km^2, maximum depth 36 m, and average summer trophogenic total P concentration 11 $mg.m^{-3}$). The bottom of the trophogenic zone, defined as the depth to 1% of surface penetrating irradiance, was at 12 m during the summers of 1985 and 1986 (A. M. Trimbee and E. E. Prepas, unpubl. data). The thermocline was at 6-m depth during the summers of 1985 and 1986. Since most algae (determined as chlorophyll *a* concentration per m^3) were below

the epilimnion (Prepas and Trew 1983), P release into trophogenic lakewater from sediments below the thermocline could affect algal biomass. Therefore, I defined shallow sediments as those that extended from the lake shore to the bottom of the trophogenic zone. Shallow sediments represented 47% of the surface area of the lake. Aquatic macrophytes were restricted to the littoral zone, less than 15-16% of the lake surface area. The maximum depth of macrophyte colonization was between 5 and 6 m; however, most macrophytes were found between 0 and 3 m depth.

Porewater collection and analyses

Sediment porewater was collected in situ with Plexiglass peepers, fitted with Gelman HT-450 membrane filters, from May to August in 1985 and 1986. Peepers used in 1985 had 140 chambers, spaced 1 cm apart, in two columns (Hesslein 1976). Smaller peepers with 25 chambers per side, spaced 1 cm apart, were used in 1986 and were especially useful in shallow, sandy sediments.

Peepers were prepared as outlined in Carignan (1984b) with the following modification: peepers were transported from the lab to the lake wrapped in two plastic bags, both of which were flushed with N_2 to remove O_2, purged and filled with N_2 to keep O_2 out. The peepers were placed in the lake sediment and retrieved by SCUBA divers. Five to ten chambers were left above the sediment-water interface to equilibrate with lakewater immediately above the sediments. Water in the peeper chambers was withdrawn with syringes within 5 to 10 min of peeper retrieval and placed in prepared serum vials. Vials were pre-washed in 3% HCl, washed with double-distilled water (DDW), and dried; in a glovebag, they were flushed and filled with N_2, and capped with Wheaton

stoppers. The pressure in the vials was maintained from the time water samples were injected into the vials until the samples were analyzed. Therefore, I assume that diffusion of gases through the stoppers was minimal. Peepers and porewater samples were handled in a N_2 environment to reduce loss of dissolved P by chemical precipitation caused by changes in redox potential (Bray et al. 1973; Troup et al. 1974).

Because the peepers had chambers in two columns, water samples from both sides of the peeper were analyzed separately; thus, duplicate P profiles were obtained for each peeper. The volume required for porewater analyses was 6 mL. Since each chamber contained about 3 mL, it was necessary to pool samples from adjacent chambers below the sediment-water interface. The samples above the sediment-water interface were more dilute than porewater; water from all chambers above the sediment-water interface were pooled. Unless otherwise indicated, the following samples were collected per side: (1) one lakewater sample pooled from all chambers above the sediment-water interface, (2) five porewater samples from 0 to 10 cm in the sediment at 2-cm intervals, and (3) nine porewater samples from 10 to 55 cm in the sediment at 5-cm intervals for the long peepers or one sample from 10 to 15 cm in the sediment for the small peepers.

Porewater and lakewater from the serum vials were subsampled within 2 h after collection, diluted 5 to 25 times with DDW, and analyzed for soluble reactive P (SRP) within 12 h after collection (Murphy and Riley 1962). Samples from five peepers were also analyzed for total dissolved P (TDP); concentrations of SRP were 94 to 100% of TDP. Since the difference between SRP and TDP concentrations was small, samples were routinely analyzed according to the less time-consuming SRP analyses.

All peeper and sample preparation as well as chemical analyses were performed at the Meanook Biological Research Station, located 15 km from Narrow Lake.

Evaluation of porewater collection and analysis

Peepers were placed at depths of 4 and 15 m in one transect (A in Fig. 2.1) during May, 1985 to determine the time required for peeper equilibration (i.e., time when P concentrations within peepers were equal to those in porewater). Peepers were retrieved after 1, 3, 6, 9, 11, 17, 25, and 31 d at the 4-m site and after 6, 13, 14, 24, and 27 d at the 15-m site. For each site, comparisons between porewater SRP concentrations ([SRP]) after different installation times were non-orthogonal; therefore, ANOVAs were performed with different probabilities than for orthogonal comparisons (i.e., experimentwise error rate a; Sokal and Rohlf 1981, p242). First, [SRP] from consecutive dates were compared; the equilibration time was chosen as the number of days after which [SRP] remained the same. Two additional non-orthogonal comparisons were performed to determine whether [SRP] were (1) significantly less before equilibration time and (2) similar after equilibration time, relative to those at equilibration time.

To determine the effect of sampling delay on porewater [SRP], a 0.5-mL sample was removed from each chamber of a peeper at four time intervals (0, 10, 20, and 30 min after retrieval); the peeper was equilibrated at 7.5-m depth and collected in August, 1986. Porewater was pooled from 5-cm sections of the peeper to obtain an adequate aliquot for SRP analyses. Samples were placed directly into culture tubes for subsequent analyses. These samples were also used to test

differences in porewater [SRP] between the two sides of the peeper. The comparisons of [SRP] after different time intervals were non-orthogonal; concentrations after different sampling delays were compared as for peeper equilibration time.

To test the effect of laboratory subsampling and dilutions on porewater [SRP], porewater was retrieved from 15-m depth on two separate occasions in 1985. Twenty mg $P.m^{-3}$ was added to culture tubes with porewater aliquots, and [SRP] between tubes with and without P additions were compared.

Temporal and spatial variability of porewater SRP

To examine temporal changes in porewater [SRP], porewater samples were collected every second week from May to August, 1986. At least one peeper was installed at three sites (Fig. 2.1): one shallow (2.5 m) with macrophytes (Vallisneria sp) and one deep (7.5 m), both located on transect A, and one shallow without macrophytes (3 m, site E).

To determine spatial variability in porewater [SRP], 15 peepers were placed at 11 sites, all at 5-m depth. Five peepers were placed close together (<0.15 m^2) on transect A (Fig. 2.1), while one peeper was placed at each of 10 additional sites (D, Fig. 2.1). These sites were equidistant along the length of Narrow Lake, alternating on east and west shores. To minimize the impact of temporal changes on porewater [SRP], all 15 peepers were retrieved and analyzed on August 14 and 15, 1986. Porewater [SRP] from the five peepers on transect A were also used to test normality and homogeneity of sample variance.

To investigate variability of porewater [SRP] with lake depth, one peeper each was placed at 3-, 7-, 10-, and 15-m depths along three transects. The transects covered both sides and basins of Narrow Lake

and were perpendicular to the shore (A, B, and C, Fig. 2.1). Peepers were installed in each of the three transects, two or three times over the summer of 1985. In addition, peepers were installed at 4-m depth in transect A, 5 times during 1985. Peepers were also installed in transect A during the summer of 1986 at the following depths: (1) 2.5, 5, 7.5, and 10 m (twice) and (2) 1, 2.5, 4, 5, 6, 7.5, 9, 10, and 11 m (once). In total, porewater [SRP] were determined from 44 peepers from these three transects: 28 and 16 peepers in 1985 and 1986, respectively. Of 28 peepers sampled in 1985, 18 were located in shallow sediments; all peepers in 1986 were located in shallow sediments.

Statistical tests were performed according to Sokal and Rohlf (1986) and Snedecor and Cochran (1980). Differences in porewater [SRP] over the summer and with depth of the water column were determined on porewater in the top 15 and 5 cm of the sediment, respectively. Concentrations in the top 5 cm of the sediment were calculated as a weighted average of three samples from the top 6 cm in the sediment. This stratum was chosen because it was within the most active layer contributing P to the overlying water, i.e., the top 10 cm of the sediment (Tessenow 1972; Schindler et al. 1977). Deeper sections were analyzed to determine a potential source of P to the top 5-cm section.

SRP release from shallow sediments into lakewater

Molecular diffusion of SRP across the sediment-water interface was calculated according to Eq. 1 (Berner 1980):

$$J = \phi \cdot D \cdot \theta^{-2} \cdot dC/dx \qquad (1),$$

in which J is the SRP flux across the sediment-water interface, ϕ is the

water content by volume (0.57; unpubl. data), D is the molecular diffusion coefficient (1.24×10^{-9} $m^2.s^{-1}$; Quigley and Robbins 1986), θ^2 is the tortuosity term ($\phi^{-0.8}$; Berner 1980), and dC/dx is the SRP gradient across the sediment-water interface. SRP gradients were calculated between [SRP] in the top 5 cm of the sediment and the overlying lakewater at sites from transects A, B, and C (Fig. 2.1). Concentrations of SRP 0.5 cm above the sediment-water interface were assumed to equal [SRP] measured from 0 to 10 cm above the interface. To calculate J, shallow sediments were divided in a 0-3 m depth stratum (where macrophytes were abundant) and a 3-12 m stratum (where macrophytes were scarce or absent). Average SRP gradients were calculated for each stratum and pooled, weighted for sediment area.

2.4 RESULTS

Evaluation of porewater collection and analysis

Equilibration time for [SRP] in the peepers was determined at two sites, 4 and 15 m. At the 4-m depth, porewater [SRP] in the top 50 cm of the sediment increased during the first 17 days and did not change during the subsequent 14 days (non-orthogonal comparisons; df = 63, t = 116 and 0.08, a < 0.01 and > 0.1, respectively). The average porewater [SRP] in the top 50 cm of the sediment was 42 $mg.m^{-3}$ after 11 days, increased to 78 $mg.m^{-3}$ after 17 d, and remained similar, at 72 $mg.m^{-3}$, after 31 d (Fig. 2.2a). At the 15-m site, porewater [SRP] increased significantly from 6 to 13 d and did not change significantly from 13 to 31 days (df = 36, t = 8.2 and 0.31, a < 0.01 and > 0.1, respectively). The average porewater [SRP] in the top 50 cm of the sediment at 15-m

depth was 815 $mg.m^{-3}$ after 6 d, increased to 1890 $mg.m^{-3}$ after 13 d, and remained unchanged at 1883 $mg.m^{-3}$ after 31 d (Fig. 2.2b). Equilibration time (17 and 13 d at 4- and 15-m depth, respectively) differed only by 4 d between the two sites; both were well within the range of 3 to 20 d determined by Carignan (1984b, 1985). Consequently, all peepers at Narrow Lake were equilibrated in the sediment for a minimum of two weeks before they were sampled.

I determined the effect of sampling delay (0, 10, 20, and 30 min) on porewater [SRP] from a peeper installed at 7.5-m depth. [SRP] in porewater and in lakewater just above the sediment-water interface from the two sides were not significantly different (paired t-test; df = 15, t = 1.43, P > 0.2; data from four different time periods and four depths in the sediment were included in the analysis). Therefore, [SRP] from two sides of the peeper were pooled. The pooled porewater [SRP] tended to decrease over 30 min (on average 8%); the decrease was significant (2-way ANOVA; df = 3,6, F = 6.26, P < 0.05). Porewater [SRP] did not differ between 0 and 10 min after peeper retrieval (non-orthogonal comparisons; df = 6, t = 1.97, a > 0.05). Porewater [SRP] were significantly less after 20 and 30 min compared to 0 min after peeper retrieval from the sediment (df = 6, t = 3.493 and 3.906, respectively, a < 0.025). Subsampling of the peepers (except the deepest 30 cm of the large peepers) was completed within 5 to 10 min of retrieval from lake sediments; these porewater [SRP] were not affected by a delay in sampling.

The recovery of 20 $mg.m^{-3}$ standard P additions was not affected by subsampling and dilutions in both peepers (paired t-tests difference = 20 mg $P.m^{-3}$; df = 11, t = 1.64, P > 0.2, and df = 22, t = 1.98,

$P > 0.1$).

Porewater [SRP] increased with depth in the sediment in 52 of 71 peepers collected at Narrow Lake during 1985 and 1986 (all equilibrated peepers: paired t-test, $P < 0.025$, Fig. 2.3). Therefore depth in the sediment was treated as a block in subsequent analyses of spatial and seasonal variability of [SRP]. [SRP] were similar for both sides of 51 of these 71 peepers ($P > 0.025$). Average [SRP] of the two sides were used in further analyses to reduce the variability of the SRP data (unless otherwise indicated).

In 1986, normality of porewater [SRP] and homogeneity of variance were evaluated with five peepers spaced close together ($0.15 m^2$) at 5-m depth (Transect A, Fig. 2.1). To increase the sample size, data from two sides of the peeper were analyzed separately. The average [SRP] in lakewater just above the sediment-water interface was 3 $mg.m^{-3}$. Porewater [SRP] increased from 41 $mg.m^{-3}$ in the top 2 cm of the sediment to 121 $mg.m^{-3}$, 10 to 15 cm below the sediment-water interface. Porewater [SRP] varied by three- to four-fold within each sediment depth (Table 2.1). When [SRP] in lakewater just above the sediment-water interface and in porewater from each sediment depth were tested for normality, five of seven sections followed a normal distribution (above the sediment-water interface, and 0-2, 4-6, 6-8, 10-15 cm in the sediment; Kolmogorov-Smirnov test, $n = 10$, $P > 0.1$). [SRP] in the other two sections (2-4 and 8-10 cm in the sediment) were slightly different from a normal distribution ($0.05 > P > 0.01$). Overall, variance of porewater [SRP] from the small site was homogeneous (F_{max} test, df = 6,9, $F_{max} = 4.77$, $P > 0.05$).

In summary, porewater [SRP] equilibrated within two weeks after

installation of the peeper. [SRP] in this equilibrated porewater were not affected by: (1) sampling delay of 10 min (after retrieval from the bottom sediments) and (2) subsampling and diluting for chemical analyses. In addition, porewater [SRP] met two important conditions for parametric statistical analyses: normality and homogeneity of variance.

Temporal and spatial variability of porewater SRP

Comparisons of porewater [SRP] in the top 15 cm of the sediment at three sites (shallow with macrophytes, shallow without macrophytes, and deep) showed significant temporal changes from mid-May to mid-August, 1986 (2-way ANOVA; $P < 0.01$). At the shallow site with macrophytes (2.5 m transect A), porewater [SRP] in the top 5 cm of the sediment first increased from May to June and then decreased after June 22, 1986 (Fig. 2.4). In contrast, porewater [SRP] at the shallow site without macrophytes (site E) increased during June, decreased from June to July, and then increased after July 11, 1986 (Fig. 2.4). Porewater [SRP] decreased from May to June and increased from June to August at the deep site (7.5 m transect A; Fig. 2.4). At all three sites, temporal changes in porewater [SRP] at depths greater than 5 cm below the sediment-water interface were similar to the trends observed for the top 5 cm in the sediment (Fig. 2.4).

Average porewater [SRP] in the top 15 cm of the sediment were lower at one site (Transect A, Fig. 2.1; 99 $mg.m^{-3}$) than at 10 other sites over the entire lake (D, Fig. 2.1; 168 $mg.m^{-3}$). Porewater [SRP] from each section in the sediment were also significantly lower in peepers placed close together than those placed over the entire lake (2-way ANOVA; df = 1,5, $F = 29.37$, $P < 0.005$). Although the standard deviation of porewater [SRP] within each sediment depth was lower in the small

site than over the entire lake (Table 2.1), overall variance was not significantly different (2-level nested ANOVA with unequal sample size, within and between sites as groups, and depth in the sediment as subgroups; df = 1,10, F = 4.50, P > 0.05).

Porewater [SRP] in the top 5 cm of the sediment increased with depth of the water column (Fig. 2.5). Porewater [SRP] in macrophyte sites were much greater than those at sites without macrophytes; data from the macrophyte sites were excluded in the following analyses. A highly significant relationship was found between porewater [SRP] and depth (Fig. 2.5; df = 38, r^2 = 0.63, P < 0.0001). The relationship between porewater [SRP] in shallow sediments and depth was also significant (df = 28, r^2 = 0.37, P < 0.001).

SRP release from shallow sediments into lakewater

At sites less than 12-m depth located in transects, [SRP] in lakewater above the sediment-water interface varied from 1 to 14 $mg.m^{-3}$. Porewater [SRP] in the top 5 cm of the sediments varied from 5 to 374 $mg.m^{-3}$ and was, on average, 13 times greater than [SRP] in lakewater just above the sediment-water interface. When sites colonized by macrophytes were excluded, SRP gradients across the sediment-water interface increased with depth (Fig. 2.5; df = 28, r^2 = 0.33, P < 0.001); the average SRP gradient according to this relationship for depths from 3 to 12 m was 22.4 $mg.m^{-3}.cm^{-1}$. At sites colonized by macrophytes (depths from 0 to 3 m), the average SRP gradient across the sediment-water interface was 53.3 $mg.m^{-3}.cm^{-1}$. Overall, the average SRP gradient across the sediment-water interface of shallow sediments was 28.8 $mg.m^{-3}.cm^{-1}$; SRP release from shallow sediments to lakewater by molecular diffusion was 0.11 $mg.m^{-2}.d^{-1}$.

2.5 DISCUSSION

To date, there is little information on variation in porewater [SRP] over the summer, within a single depth, and between depths in one lake. Observations of seasonal trends in porewater [SRP] during spring and the open water season are limited to lakes where porewater was collected once per month and mostly from sites colonized by macrophytes (Holdren at al. 1977; Carignan 1985; Smith and Adams 1986).

At Narrow Lake, porewater [SRP] in the top 5 cm of the sediment first increased and then decreased over the summer at a shallow site with macrophytes. Porewater [SRP] at a macrophyte site in Lake Wingra (a shallow, eutrophic lake) decreased and then increased over the summer (Smith and Adams 1986). In contrast, porewater [SRP] in a macrophyte bed at Lake Memphremagog (a large mesotrophic lake) did not change over the summer in the top 5 cm of the sediment, but appeared to decrease from 5 to 38 cm in the sediment (Carignan 1985). The contradicting trends observed in porewater SRP at lakes Narrow, Wingra, and Memphremagog may be caused by differences in macrophytes and sediment characteristics. The aquatic macrophyte at Narrow Lake was Valisneria sp.; in lakes Wingra and Memphremagog it was Myriophyllum spicatum. Exchangeable P and porewater pH may differ in the three lakes. Because exchangeable P in particulate sediments may buffer porewater [SRP] and porewater [SRP] depend partly on pH (Ku et al. 1978; Carignan 1985), differences in exchangeable P and porewater pH may explain the different trends of porewater SRP over the summer.

Trends of porewater [SRP] over the summer also differed between sites colonized by macrophytes and those without macrophytes. At Narrow

Lake, porewater [SRP] decreased from late June to August in a site colonized by macrophytes and varied inconsistently in a site without macrophytes. These trends are similar to those observed in Lake Memphremagog (Carignan 1985), where areas cleared of macrophytes were compared to non-cleared sites. Uptake of P by macrophyte roots during the macrophyte growing season may explain different patterns in porewater SRP concentrations over the summer at sites with and without macrophytes (Carignan 1985). At Narrow Lake, porewater [SRP] in the shallow site with macrophytes were higher than in the site without macrophytes. The presence of macrophytes may increase P deposition and decrease mixing of porewater with lakewater. Increased mineralization of sedimented material and decreased mixing between porewater and lakewater could increase porewater [SRP] (Carignan 1984a).

At two depths in Narrow Lake not colonized by macrophytes, no trends in porewater [SRP] from late June to August were observed (Fig. 2.4). These patterns were somewhat different from those observed at two sites, not colonized by macrophytes, in Lake Mendota (Holdren et al. 1977). At Lake Mendota, porewater [SRP] increased over the summer at the shallow site, whereas they did not change at deep site. Trends in porewater [SRP] over the summer may differ at the two lakes due to sediment P release. Mixing, pH, redox potential and particulate sediments influence P release from sediments (Bostrom et al. 1982); these processes may be different at the two lakes.

At Narrow Lake, variance of [SRP] over the entire porewater profile was not significantly different between a small site ($< 0.15\ m^2$) and the entire lake. Although, average porewater [SRP] were higher over the entire lake than within the small site, differences between [SRP] in the

top 5 cm of the sediment were not significant (t-test; df = 13, t = 1.1, $P > 0.2$). Porewater [SRP] in another lake varied one order of magnitude in three sites far apart but at similar depth (Drake and Heany 1987). Carignan (1985) also found substantial variation in porewater [SRP] from four peepers within one site.

A strong relationship between porewater [SRP] and depth at Narrow Lake was evident when data from macrophyte sites were excluded (Fig. 2.5). Relationships between porewater [SRP] and depth were similar during 1985, and in 1985 and 1986 (ANCOVA; residual variance $P > 0.25$, slope $P > 0.5$, intercept $P > 0.5$). Differences in the relationship between porewater [SRP] and depth in three transects, sampled in 1985, were tested. Although the three transects were far apart, the relationship between lake depth and porewater [SRP] (in the top 5 cm of the sediment) were very similar (ANCOVA; residual variances, slopes, and elevations: $P > 0.5$). Presence of macrophytes can obscure trends with depth (Holdren et al. 1977; Carignan 1984a). To my knowledge, the consistent increase of porewater [SRP] with lake depth at Narrow Lake is the first significant relationship reported in the literature, although other data are consistent with this trend (Bannerman et al. 1974; Holdren et al. 1977; Carignan 1984a; Psenner and Pucsko 1988).

During summer, release of SRP from shallow sediments in Narrow Lake averaged 0.11 $mg.m^{-2}.d^{-1}$. The contribution of P from the sediments in the trophogenic zone (46.8% of lake surface area) to the entire lake was 0.05 $mg.m^{-2}.d^{-1}$. The contribution of SRP from sediments to overlying water is underestimated by this calculation since the gradients are (1) likely much steeper just below the sediment-water interface, and (2) release is enhanced in shallow sediments by bioturbation, mixing, and

groundwater flow. Even so, our conservative estimate of P release rate from shallow sediments is 29% of the P input by atmospheric deposition from May to August (0.18 $mg.m^{-2}.d^{-1}$, Shaw et al. 1989). Narrow Lake has a small drainage basin (7 km^2) and beaver dams limit runoff from its watershed (the lake level is consistently lower than the water level at the other side of the dams). Thus, atmospheric deposition is the major external input of P to the lake. SRP release from shallow sediments into lakewater represents at least one fourth of the major external source of P to Narrow Lake.

To calculate P release from shallow sediments directly into the epilimnion, a sampling design to monitor porewater P should focus on sediments in the trophogenic zone with and without macrophytes. At Narrow Lake, average [SRP] in the top 5 cm of the sediment and variance at the 5-m depth were not statistically different between either a small site and the entire lake, or four depths in three transects. However, porewater [SRP] increased substantially with lake depth. Sampling effort could thus be limited to one transect. Based on the Narrow Lake data, the required number of peepers for the top 5 cm in the sediment at one site was seven (calculated from the small-site data Table 2.1, with a desired ratio of SE to mean of 50% and a 90% confidence interval). Since [SRP] increased with lake depth, porewater should be collected at three or more depths in a transect. At a deep site, sampling may be restricted to one date during the summer. However, samples should be collected at least monthly from shallow sites because temperature and macrophytes may influence porewater [SRP].

Summer and spatial trends of porewater SRP at Narrow Lake were used to derive a strategy to sample porewater efficiently. At Narrow Lake,

calculation of a P release rate was feasible; this release was important relative to the major external P source. More information is needed on a range of lake types to determine the generality of the seasonal and spatial trends in porewater SRP observed at Narrow Lake and the impact of P release from shallow sediments into aerobic lakewater at other lakes.

2.6 REFERENCES

Andersen, J. M. 1975. Influence of pH on release of phosphorus from lake sediments. Arch. Hydrobiol. 76:411-419.

Bannerman, R. T., D. E. Armstrong, G. C. Holdren, and R. T. Harris. 1974. Phosphorus mobility in Lake Ontario. p. 158-178. In Proceedings of the 17th Conference on Great Lakes Research, Ann Arbor, MI. 850p.

Banoub, M. W. 1975. Experimental studies on material transactions between mud and water of the Gnadensee (Bodensee). Verh. Internat. Verein. Limnol. 19:1263-1271.

Berner, R. A. 1980. Early diagenesis. Princeton Univ. Press, Princeton, NJ. 241p.

Bostrom, B., M. Jansson, and C. Forsberg. 1982. Phosphorus release from lake sediments. Arch. Hydrobiol. 18:5-59.

Bray, J. T., O. P. Bricker, and B. N. Troup. 1973. Phosphate in interstitial waters of anoxic sediments: oxidation effects during sampling procedure. Science 180:1362-1364.

Carignan, R. 1984a. Sediment geochemistry in a eutrophied lake colonized by the submerged macrophyte Myriophyllum spicatum. Verh. Internat. Verein. Limnol. 22:355-370.

Carignan, R. 1984b. Interstitial water sampling by dialysis: methodological notes. Limnol. Oceanogr. 29:667-670.

Carignan, R. 1985. Nutrient dynamics in a littoral sediment colonized by the submerged macrophyte Myriophyllum spicatum. Can. J. Fish. Aquat. Sci. 42:1303-1311.

Carignan, R., and J. O. Nriagu. 1985. Trace metal deposition and

mobility in the sediments of two lakes near Sudbury, Ontario. Geochim. Cosmochim. Acta 49:1753-1764.

Drake, J. C., and S. I. Heany. 1987. Occurrence of phosphorus and its potential remobilization in the littoral sediments of a productive English lake. Freshwater Biol. 17:513-523.

Einsele, W. 1936. Uber die Beziehungen des Eisenkreislaufs zum Phosphatkreislauf im eutrophen See. Arch. Hydrobiol. 29:664-686.

Einsele, W. 1938. Uber Chemische und Kolloidchemische Vorgange in Eisen-Phosphatsystemen unter limnochemischen und limnogeologischem Gesichtspunkten. Arch. Hydrobiol. Plankt. 33:361-387.

Einsele, W., and H. Vetter. 1938. Untersuchungen uber die Entwicklung der physikalischen und chemischen Verhaltnisse im Jahreszyklus in einem massig eutrophen See (Schleinsee bei Langenargen). Int. Rev. ges. Hydrobiol. 36:285-324.

Gallepp, G. W. 1979. Chironomid influence on phosphorus release from sediment-water microcosms. Ecology 60:547-556.

Green, R. 1972. Geological map of Alberta. Research Council of Alberta map (scale 1:1,267,000), Edmonton, Alta.

Hesslein, R. 1976. An in situ sampler for close interval porewater studies. Limnol. Oceanogr. 21:912-914.

Holdren, G. C., and D. E. Armstrong. 1980. Factors affecting phosphorus release from intact lake sediment cores. Environ. Sci. Technol. 14: 79-87.

Holdren, G. C., D. E. Armstrong, and R. F. Harris. 1977. Interstitial inorganic phosphorus concentrations in Lakes Mendota and Wingra. Water Res. 11:1041-1047.

Imboden, D. M., and S. Emerson. 1978. Natural radon and phosphorus as

limnologic tracers: horizontal and vertical eddy diffusion in Greifensee. Limnol. Oceanogr. 23:77-90.

Kamp-Nielsen, L. 1975. A kinetic approach to the aerobic sediment-water exchange of phosphorus in Lake Esrom. Ecol. Modelling 1:153-160.

Kawai, T., A. Otsuki, M. Aizaki, and M. Nishikawa. 1985. Phosphate release from sediment into aerobic water in a eutrophic shallow lake, L. Kasumigaura. Verh. Internat. Verein. Limnol. 22: 3316-3322.

Kjearsgaard, A. A. 1972. Soil Survey of Tawatinaw (83-I). Univ. of Alberta Bull. No. SS-12, Edmonton, Alta. 103p.

Kortmann, R. W., D. D. Henry, A. Kuether, and S. Kaufman. 1982. Epilimnetic nutrient loading by metalimnetic erosion and resultant algal responses in Lake Waramaug, Connecticut. Hydrobiologia 92:501-510.

Ku, W. C., F. A. DiGiano, and T. H. Feng. 1978. Factors affecting phosphate adsorption equilibria in lake sediments. Water Res. 12:1069-1074.

Lee, G. F., W. C. Sonzogni, and R. D. Spear. 1977. Significance of oxic vs anoxic conditions from Lake Mendota sediment phosphorus release. p. 294-306. In H. L. Golterman (ed.). Interactions between sediments and freshwater (Proc. SIL-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands. 473p.

Mortimer, C. H. 1941. The exchange of dissolved substances between mud and water in lakes. J. Ecol. 29:280-329.

Mortimer, C. H. 1942. The exchange of dissolved substances between mud and water in lakes. J. Ecol. 30:147-201.

Murphy, J., and J. P. Riley. 1962. A modified single solution method for

the determination of phosphate in natural waters. Anal. Chim. Acta 27:31-36.

Nurnberg, G. K. 1984. The prediction of internal phosphorus load in lakes with anoxic hypolimnia. Limnol. Oceanogr. 29:111-124.

Ohle, W. 1937. Kolloidgele als Nahrstoffregulatoren der Gewasser. Naturwissenschaften 25:471-474.

Prepas, E. E., and D. O. Trew. 1983. Evaluation of the phosphorus-chlorophyll relationship for lakes off the Precambrian Shield in Western Canada. Can. J. Fish. Aquat. Sci. 40:27-35.

Psenner, R., and R. Pucsko. 1988. Phosphorus fractionation: advantages and limits of the method for the study of sediment P origins and interactions. Arch. Hydrobiol. Beih. 30:43-59.

Quay, P. D., W. S. Broecker, R. H. Hesslein, and D. W. Schindler. 1980. Vertical diffusion rates determined by tritium tracer experiments in the thermocline and hypolimnion of two lakes. Limnol. Oceanogr. 25:201-218.

Quigley, H. A., and J. A. Robbins. 1986. Phosphorus release processes in nearshore southern Lake Michigan. Can. J. Fish. Aquat. Sci. 43:1201-1207.

Riley, E. T., and E. E. Prepas. 1984. Role of internal phosphorus loading in two shallow, productive lakes in Alberta, Canada. Can. J. Fish. Aquat. Sci. 41:845-855.

Rippey, B. 1977. The behaviour of phosphorus and silicon in undisturbed cores of Lough Neagh sediments. p. 345-353, In H. L. Golterman (ed.). Interactions between sediments and freshwater (Proc. SIL-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands. 473p.

Schindler, D. W. 1977. Evolution of phosphorus limitation in lakes.

Science 195:260-262.

Schindler, D. W., R. Hesslein, and G. Kipphut. 1977. Interactions between sediments and overlying waters in natural oligotrophic and experimentally-eutrophied Precambrian Shield lakes. p. 235-243. In H. L. Golterman (ed.). Interactions between sediments and freshwater (Proc. SIL-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands. 473p.

Schindler, D. W., T. Ruszczynski, and E. J. Fee. 1980. Hypolimnion injection of nutrient effluents as a method for reducing eutrophication. Can. J. Fish. Aquat. Sci. 37:320-327.

Shaw, R. D., A. M. Trimbee, A. Minty, H. Fricker, and E. E. Prepas. 1989. Atmospheric deposition of phosphorus and nitrogen in central Alberta with emphasis on Narrow Lake. Water, Air and Soil Pollut. 42. In press.

Smith, C. S., and M. S. Adams. 1986. Phosphorus transfer from sediments by Myriophyllum spicatum. Limnol. Oceanogr. 31:1312-1321.

Snedecor, G. W., and W. G. Cochran. 1980. Statistical methods. 7th ed. Iowa State Univ., IA.

Sokal, R. R., and F. J. Rohlf. 1981. Biometry. 2nd ed. Freeman, San Francisco, CA. 859p.

Stauffer, R. E., and D. E. Armstrong. 1984. Lake mixing and its relationship to epilimnetic phosphorus in Shagawa Lake, Minnesota. Can. J. Fish. Aquat. Sci. 41:57-69.

Strong, W. L. and K. R. Leggat. 1981. Ecoregions of Alberta. Alberta Energy and Natural Resources, ENR Technical Rep. No. T/41, Edmonton, Alta. 64 p.

Syers, J. K., R. F. Harris, and D. E. Armstrong. 1973. Phosphate

chemistry in lake sediments. J. Env. Qual. 2:1-14.

Tessenow, V. 1972. Losungs-, Diffusions- and Sorptions-Prozesse in der Oberschicht von Seesedimenten. Part 1. Arch. Hydrobiol. Suppl. 38:353-398.

Troup, B. N., O. P. Bricker, and J. T. Bray. 1974. Oxidation effect on the analysis of iron in the interstitial water of recent anoxic sediments. Nature 249:237-239.

Ulen, B. 1978. Seston and sediment in Lake Norrviken 3: Nutrient release from sediment. Schweiz. Z. Hydrol. 40:287-305.

Van Liere, L., and L. R. Mur. 1982. The influence of simulated groundwater-movement on the phosphorus release from sediments, as measured in a continuous flow system. Hydrobiologia 92:511-518.

Table 2.1: Mean, range and standard deviation (SD) of soluble reactive phosphorus concentrations (SRP, in $mg.m^{-3}$) in lakewater just above the sediment-water interface (-10 - 0 cm) and in porewater from the top 15 cm of the sediment from a lake depth of 5 m at Narrow Lake collected in August 1986.

	SRP					
	Within 0.15 m^2 (n=5)			Entire lake (n=10)		
Depth in the sediment (cm)	mean	range	SD	mean	range	SD
-10 - 0	3	2 - 4	1.1	3	1 - 5	1.3
0 - 2	41	20 - 85	25.5	49	7 - 150	47.0
2 - 4	71	41 - 137	39.8	137	13 - 368	104.2
4 - 6	106	48 - 223	70.3	176	32 - 522	144.3
6 - 8	107	61 - 196	53.9	192	51 - 576	153.4
8 - 10	112	78 - 186	45.3	202	54 - 538	134.5
10 - 15	121	69 - 195	49.6	202	44 - 509	125.0

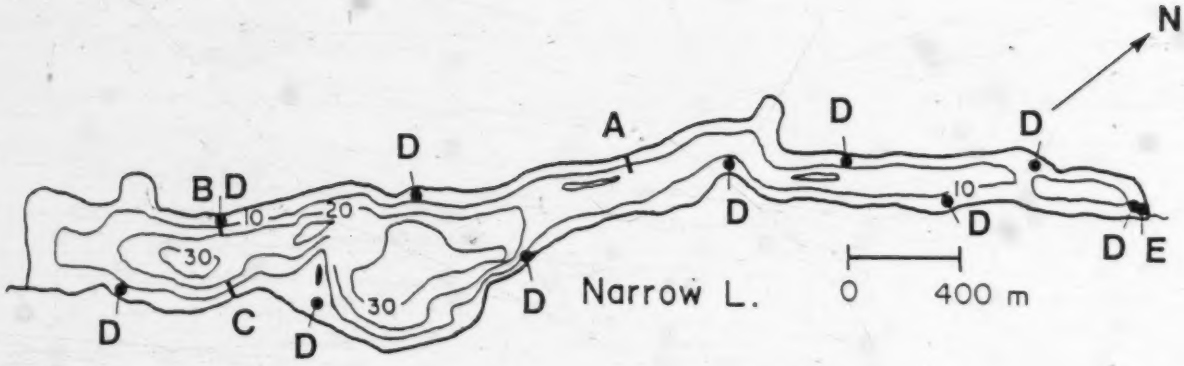
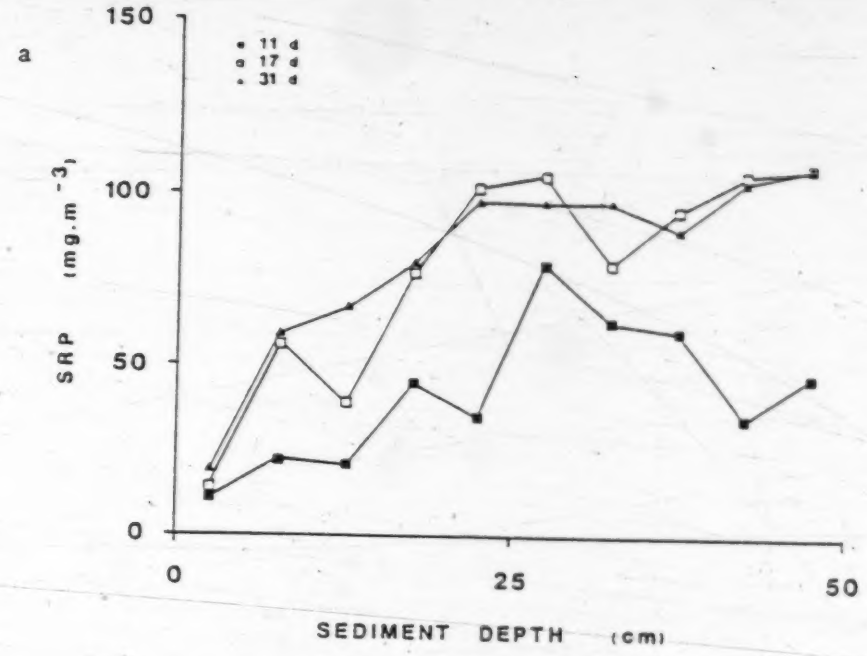


Figure 2.1: Peeper locations at Narrow Lake in 1985 and 1986. Peeper transects are indicated as A, B, and C, peeper sites at 5-m lake depth as D, and shallow site without macrophytes as E.



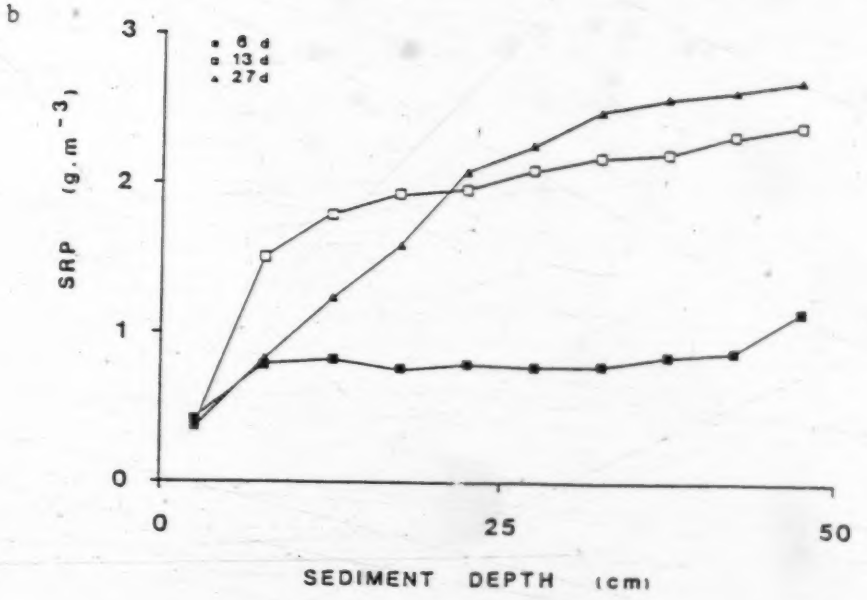


Figure 2.2: Porewater soluble reactive phosphorus (SRP) in the top 50 cm of the sediment at 4-m depth (a) and 15-m depth (b) after different incubation periods in the sediment.

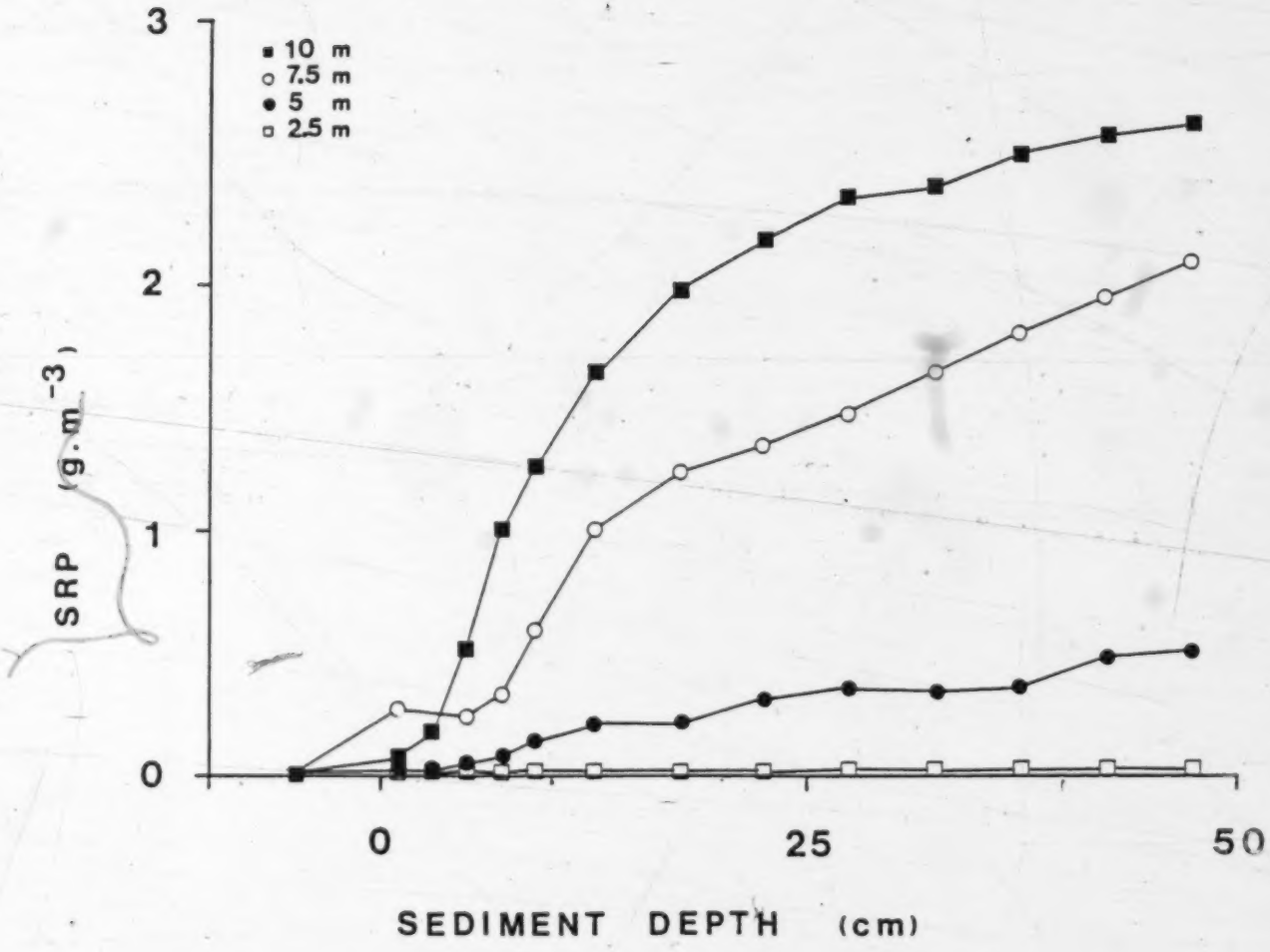


Figure 2.3: Porewater soluble reactive phosphorus (SRP) in the top 50 cm of the sediment from four lake depths collected on July 24-25, 1985.

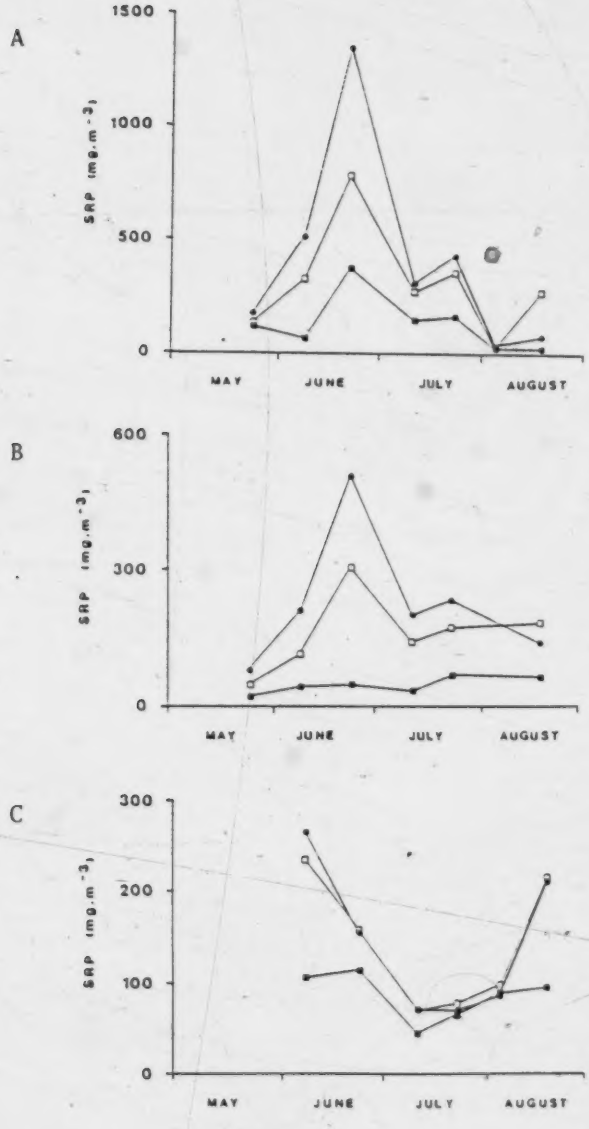


Figure 2.4: Porewater soluble reactive phosphorus (SRP) over the summer of 1986: (a) a shallow site with macrophytes, (b) a shallow site without macrophytes, and (c) a deep site, all at Narrow Lake. Porewater SRP concentrations from three sediment sections are indicated: 0 to 5 cm (■), 5 to 10 cm (□) and 10 to 15 cm in the sediment (●).

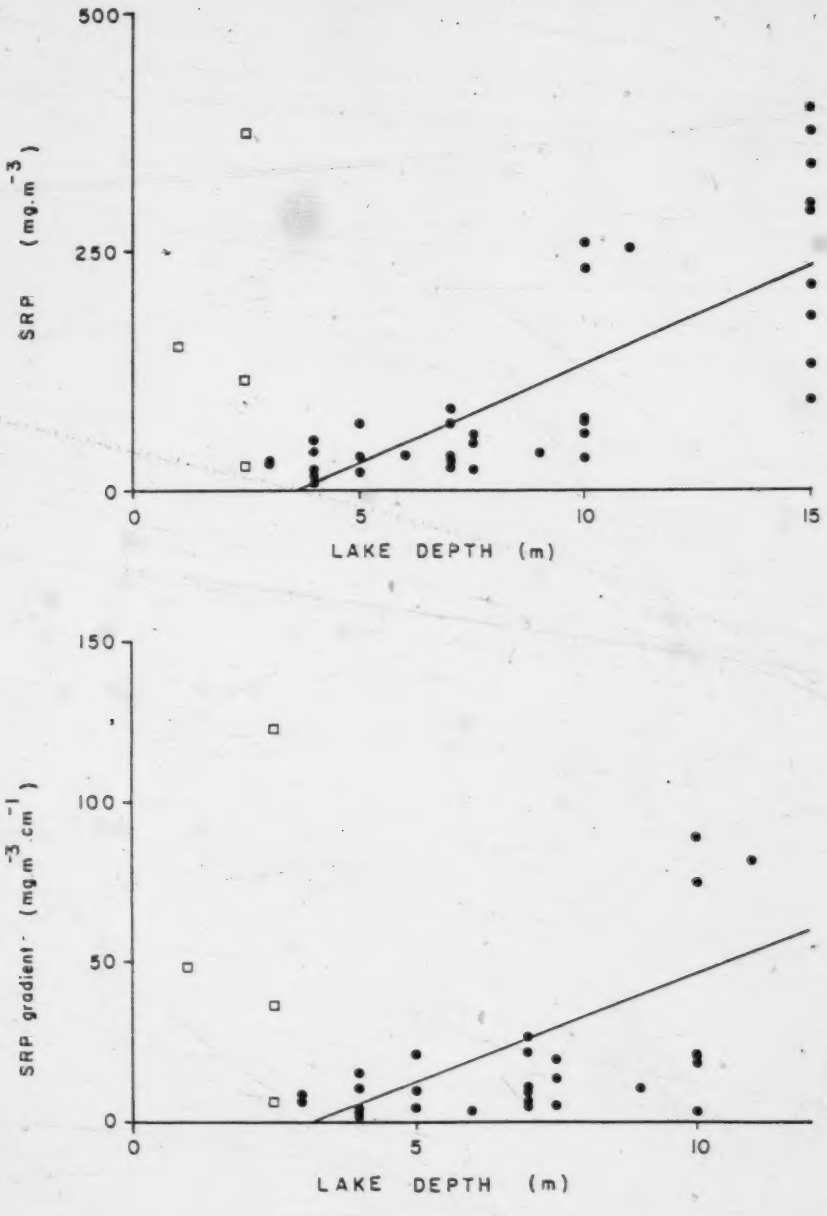


Figure 2.5: The relationship between (a) average porewater soluble reactive phosphorus (SRP) in the top 5 cm of the sediment, and (b) SRP gradients across the sediment-water interface and lake depth (in m) at Narrow Lake. Regression lines were calculated with all data collected in transects during 1985 and 1986 excluding sites colonized by macrophytes (□).

3. EXCHANGE OF PHOSPHORUS FROM SHALLOW SEDIMENTS AT NINE ALBERTA LAKES.[1]

3.1 ABSTRACT

In this study, potential exchange of phosphorus (P) between sediments and lakewater and particulate sediments and porewater was evaluated in nine eutrophic lakes in Alberta. Lakewater above the sediments, porewater and sediments were collected from shallow depths (0.5 to 10 m) during May to August, 1986. Lakewater soluble reactive P concentrations ([SRP]) were positively correlated with porewater [SRP] ($\underline{P}<0.01$) and negatively with the Fe:P molar ratio in porewater ($\underline{P}<0.001$). Potential release of SRP from sediments to lakewater (by molecular diffusion) was positively correlated with particulate P fractions that are known to exchange P with water ($\underline{P}<0.01$). In porewater, [SRP] were positively correlated with Fe^{2+} concentrations and pH ($\underline{P}<0.001$ and 0.05, respectively). These results indicate: (1) potential transport of P from sediments to lakewater when Fe is not abundant, (2) some overlap of P and Fe sources, and (3) pH partially regulates the exchange of P between particulate sediments and porewater. No significant relationships ($\underline{P}>0.05$) were found between porewater [SRP] and particulate P fractions. In this study, correlation coefficients were generally low, which suggests: (1) the chemical fractionation of particulate sediments failed to isolate the exchangeable P fraction, and/or (2) partitioning of P within sediments and the release of P from sediments to lakewater are complex processes, not regulated by pH and Fe^{2+} in porewater alone.

[1]A version of this chapter has been submitted for publication. J.F.H. Shaw and E.E. Prepas. J. Environ. Qual.

3.2 INTRODUCTION

In most lakes, phosphorus (P) is the nutrient that limits algal productivity. Simulation models have been developed to evaluate the impact of external P sources on lake eutrophication (e.g., Vollenweider, 1968). However, these models rarely include internal P sources (i.e., sediments); a common perception is that sediments are a source of P to lakes when lakewater above the sediments is anaerobic. Reducing conditions usually develop over deep (hypolimnetic) sediments. P, released from these deep sediments, is generally contained below the thermocline and may not be directly available to algae (Schindler et al., 1977; Stauffer and Armstrong, 1984). However, dependent on factors such as pH, temperature and mixing, P may also be released from sediments into aerobic lakewater (Andersen, 1975; Kamp-Nielsen, 1975; Holdren and Armstrong, 1980). Lakewater is usually aerobic over shallow sediments, i.e., those sediments in contact with trophogenic or epilimnetic lakewater. In contrast to P released from deep sediments in thermally stratified lakes, P released from shallow sediments is directly available to algae.

In bottom sediments, P is both dissolved in porewater and bound to particulate matter. Porewater P is more mobile than particulate P; porewater P may be transported to lakewater by diffusion, bioturbation, mixing and groundwater (Syers et al., 1973). If porewater in shallow sediments is an important source of P to lakes, porewater and lakewater P may be correlated. Laboratory core incubations and a field study suggest the potential for such a correlation (Theis and McCabe, 1978; Ulen, 1978; Psenner, 1984). However, the mass of P in porewater is

small compared to that in particulate sediments. Therefore, exchange of P between porewater and particulate sediments may be required to sustain P release from porewater.

Adsorption/desorption reactions are thought to regulate porewater P concentrations (Syers et al., 1973; Golterman, 1984). These adsorption/desorption reactions are fast, and depend on the nature of the sorbing surface, i.e. particulate sediments (Carritt and Goodgal, 1954; Syers et al., 1973). If adsorption/desorption regulates P exchange between particulate sediments and porewater, then P in exchangeable particulate sediments is likely correlated to P in porewater (Golterman, 1984). The objective of this study was to evaluate the potential exchange of P between: (1) sediments and lakewater, and (2) particulate sediments and porewater from shallow sites at nine lakes in central Alberta.

3.3 MATERIAL AND METHODS

Study lakes

The nine study lakes are located in central Alberta (Fig. 3.1). The lakes are situated in drift, which consists primarily of glacial till. Sand lenses are present in the watersheds of Baptiste, Island, Jenkins, Long, Minnie and Narrow lakes. Sedimentary bedrock underlies all lakes (Green, 1972; Kjearsgaard, 1972; Alberta Environment, 1986). Most lakes are in the mixed-wood section of the boreal forest; S-9 is in aspen-parkland (Strong and Leggat, 1981). There is recreational development (camps and cottages) around Baptiste, Island, Long, Narrow and Minnie lakes. The drainage basins of Figure Eight, Jenkins, Minnie,

and S-9 lakes are used partially as pasture land. Control structures are present at the outlets of Minnie and Figure Eight lakes. S-9 was formed in a depression left after strip-mining for coal; no top soil was put over the spoil (Moran et al., 1986).

During the summer, six lakes were thermally stratified, whereas Figure Eight, S-9 and Tucker lakes mixed intermittently. The surface and drainage basin area and maximum depth varied in the study lakes (Table 3.1). The trophic status of the study lakes (as determined by mean summer trophogenic P; Wetzel, 1983) ranged from meso-eutrophic to hypereutrophic (Table 3.1); mean summer chlorophyll a concentrations ranged from 3 to 172 $mg.m^{-3}$. Water in the study lakes was alkaline; Ca concentrations in the study lakes varied about 2-fold (Table 3.1).

Sampling design

Porewater and sediments were collected from shallow depths, i.e., located in the trophogenic zone or epilimnion, during May to August 1986. Generally, samples were collected from four different depths along a transect perpendicular to shore (Table 3.2). The transect location was selected to represent average lake slope (i.e., ratio of distance from shore and lake depth). In the double-basin lakes, the transects were located in the south basin (Baptiste) and the north basin (Island); morphometric and chemical characteristics are presented for these (thermally stratified) basins. Two transects were sampled at S-9 Lake. At each site, I collected five sections (at 2-cm intervals) from the top 10 cm in the sediment. The top 10 cm of sediments is the sediment layer that could potentially exchange P with overlying lakewater (Tessenow, 1972).

Porewater collection and analyses

Porewater was collected *in situ* with Plexiglass peepers (Hesslein, 1976). Each peeper had two columns of 25 chambers; midpoints of the chambers in a column were spaced 1-cm apart. The peepers were fitted with a Gelman HT-450 membrane filter and were prepared as outlined by Carignan (1984a) with some modifications (Chapter 2). At each site, two peepers were placed in the sediment and retrieved after two weeks by SCUBA divers.

Water in the peeper chambers was withdrawn with syringes and placed in N_2-filled glass serum vials for soluble reactive P (SRP) and ferrous iron (Fe^{2+}) analyses or in plastic vials for pH measurement. Water samples from both sides of the peeper were stored on ice and analyzed separately; iron and pH were determined because these parameters can affect P dynamics in sediments. Water was transferred from the peeper chambers to N_2-filled serum vials as quickly as possible (within 5 to 10 min of peeper retrieval) to prevent potential P precipitation caused by changes in redox potential (Bray et al., 1973; Troup et al., 1974). Porewater for Fe^{2+} analysis was placed in opaque N_2-filled serum vials to prevent photochemical reduction from ferric to ferrous iron.

Porewater from two adjacent chambers in a column was pooled to provide 6 mL of sample needed for chemical analyses; five porewater samples were collected from the top 10 cm of the sediment (2-cm intervals). In addition, one lakewater sample from peeper chambers within 10 cm above the sediment-water interface was collected. Aliquots from porewater and lakewater samples were diluted 5 to 50 times with double distilled water. Porewater and lakewater from one side of each peeper was analyzed for SRP (Murphy and Riley, 1962); the average SRP

concentration ([SRP]) from two peepers was used in subsequent data analyses. Water from the other side of the two peepers was analyzed for Fe^{2+} by the phenanthroline method (American Public Health Association, 1980) and pH (Beckman model 119 pH meter). Acid was added to opaque culture tubes to stabilize Fe^{2+} in air, before porewater aliquots (from the opaque N_2-filled serum vials) were added to the tubes. These samples were read five to ten minutes after reagent addition. SRP and Fe^{2+} were analyzed in duplicate; turbid samples were corrected for colour. Analyses for porewater pH, SRP, and Fe^{2+} were completed at the Meanook Biological Research Station (MBRS, Fig. 3.1). SRP and pH were determined within 12 h of peeper retrieval from all sediments; Fe^{2+} analyses were also completed within 12 h on samples collected from lakes in the Athabasca area, and within 24 h on samples from Figure Eight, Minnie, S-9 and Tucker lakes.

Potential P release from sediments by molecular diffusion (PFLUX) was calculated with SRP gradients across the sediment-water interface (between porewater from the top 10 cm in the sediment and lakewater immediately above the sediment-water interface; Chapter 2, dx = 5.5 cm), water content (by volume, corrected for tortuosity; Berner, 1980) and a molecular diffusion coefficient of $D = 1.24 \times 10^{-6}$ $cm^2.s^{-1}$ (Quigley and Robbins, 1984). Water content is defined in the next section. In addition, the molar ratio of Fe:P in porewater was calculated (RATIO); RATIO was used as an indicator of potential Fe-P sorption in aerobic water (Tessenow, 1974).

Sediment collection, analyses and evaluation

During the summer of 1986, sediments were collected at most peeper sites with Plexiglass coreliners (inner diameter = 6.6 cm) by SCUBA

divers. During April 1987, sediments were obtained from Baptiste and Minnie lakes with a benthos gravity corer (Mawhinney and Bisutti, 1987). In most cases, three cores were retrieved from each peeper site. The cores were sectioned in the field at 2-cm intervals, down to a depth of 10 cm into the lake bottom. One section per core was obtained at Tucker and S-9 lakes: the top 6 and 10 cm of sediment, respectively. The sediment sections were frozen until they were analyzed.

Water content (POR, by weight) was determined on all sediment sections in all three cores per site. Sediments were dried at 60 ^{o}C for two days to reach constant weight. Average POR of the cores from each site was used in subsequent data analyses. Water content by weight was expressed by volume with a density of 1.19 g.cm^{-3} (determined from sediment sections of several study lakes).

Since certain sediment P fractions can exchange P with porewater more readily than others, sediment P fractions were differentiated by chemical extractions. To reduce the number of sediment P analyses, one of the three cores per site was analyzed. Dried sediments were ground with mortar and pestle. Ground sediment samples (<150 um) were analyzed (in duplicate) for inorganic and organic P (Mayer and Williams, 1981). Each sample was extracted sequentially for inorganic P fractions with citrate-dithionite-bicarbonate (CDB), NaOH, and HCl. After each extraction, P was measured (i.e., CDB-P, NaOH-P and HCl-P). The sum of bioavailable CDB-P and the more labile NaOH-P is the non-apatite inorganic P fraction (NAIP); NAIP is potentially the maximum of biologically available P (Logan et al., 1979). The sum of CDB-P, NaOH-P and HCl-P equals total inorganic P (SINORG-P). In addition, each ground sediment sample was extracted with HCl, cold NaOH and hot NaOH.

The combined extract was analyzed directly as total inorganic P (INORG-P) and was also digested and analyzed for total P (TOT-P). Organic P (ORG-P) is the difference between TOT-P and INORG-P.

The mean difference between duplicates of CDB-P, NaOH-P, HCl-P, INORG-P and TOT-P of 121 sediment samples was less than 4.8%. As an internal check on the sediment analyses, SINORG-P and INORG-P were compared; the two were not significantly different (paired t-test: df = 120, t = 0.02, $P > 0.5$). In addition, three sediment samples from deep sites in Baptiste Lake and Amisk Lake (a eutrophic lake located at $54^{o}35'$ N $112^{o}37'$ W) were analyzed for NAIP and HCl-P at the National Water Research Institute with the same technique (P. Manning, unpubl. data): the results from the two laboratories were similar (paired t-test: df = 5, t = 0.72, $P > 0.5$). These comparisons indicate that my values for sediment P content are consistent with current methodology.

Data preparation

Mean (x) and standard error (SE) were calculated for porewater, lakewater and sediment parameters and were compared to data from other studies. Since most porewater and sediment parameters were very different at the only hypereutrophic lake (Figure Eight) compared to the other (meso-eutrophic to eutrophic) study lakes, parameters were transformed before correlation analysis: porewater and lakewater SRP and Fe^{2+} concentrations, RATIO and sediment CDB-P, NaOH-P, HCl-P, ORG-P and PFLUX were $\log_{10}$ transformed; since some ORG-P values were 0, 1 was added before the transformation of the variables; POR, measured as a percentage, was arcsine transformed (Sokal and Rohlf, 1981). Relationships between lakewater, porewater, sediment parameters and PFLUX were examined with product-moment correlation coefficients (Dixon,

1983). All other statistical tests are described in Sokal and Rohlf (1981).

To determine potential exchange of P between porewater and lakewater immediately above the sediment-water interface, the average porewater and sediment values per site were correlated to all lakewater parameters and PFLUX. During collection of samples from Figure Eight Lake (Aug. 25, 1986), lakewater overlying this site was anaerobic (Prepas and Murphy, 1987). Anoxia could have enhanced release of SRP and Fe^{2+} from these sediments (Mortimer, 1941). Since this was the only site with anoxic water above the sediment, it was excluded from correlation analyses between lakewater and sediment parameters; the analyses were performed on data from the remaining 26 sites.

To determine potential P exchange between specific particulate P fractions and porewater, correlations between porewater and particulate sediment parameters were calculated: (1) Correlations between all analyzed sediment parameters were investigated. The variability in these correlations include variability within sites (with depth in the sediment), between sites (with depth of the overlying lakewater), and between lakes. (2) Average values of sediment parameters in the top 10 cm of the sediment were calculated and correlated as in (1) to reduce the within site variability. These analyses were performed twice: with and without data from hypereutrophic Figure Eight Lake (number of samples for (1) 126 and 121, and (2) 27 and 26, respectively).

3.4 RESULTS AND DISCUSSION

Porewater, lakewater, and particulate sediment description

The average concentration of SRP ([SRP]) in porewater from the top 10 cm of the shallow sediments in this study varied from 68 $mg.m^{-3}$ in Narrow Lake to 3622 $mg.m^{-3}$ in Figure Eight Lake (Table 3.2). Concentrations of Fe^{2+} ($[Fe^{2+}]$) in porewater from the top 10 cm of shallow sediments varied from 166 to 1010 $mg.m^{-3}$ in Tucker and Figure Eight lakes, respectively. Average porewater pH in most lakes was 8 or less; porewater pH at Minnie and Tucker lakes was much greater, 9.5 and 9.0, respectively. Porewater [SRP] and $[Fe^{2+}]$ and most porewater pH values measured in this study were comparable to values from other lakes (Holdren et al., 1977; Ripl and Lindmark, 1979; Adams et al., 1982; Van Eck and Smits, 1984; Carignan, 1984b; Ali et al., 1988). However, porewater pH at Minnie and Tucker lakes was much higher than previously reported. At pH greater than 9, the solubility product of calcite would be surpassed at atmospheric CO_2 pressure. At Minnie Lake, porewater had a green or purple colour and a H_2S-smell, which indicated the likely presence of small (< 0.45 um) photosynthetic green and purple bacteria (Pfennig, 1978; Truper and Pfennig, 1978). These bacteria could lower CO_2 pressure and increase pH over 9. Coloured porewater was not found at Tucker Lake. However, pH in groundwater from wells near Tucker Lake has been recorded as high as 9.9.

Lakewater [SRP] and $[Fe^{2+}]$ were generally less than porewater [SRP] and $[Fe^{2+}]$, respectively. Lakewater pH was generally more basic than porewater (Table 3.2 and 3.3). Gradients of SRP across the sediment-water interface varied from -19100 to 40600 $mg.m^{-4}$ at sites in Figure

Eight and Jenkins lakes, respectively. Excluding data from Figure Eight Lake, potential P release (by molecular diffusion) from sediments into lakewater varied from 0.01 to 2.31 $mg.m^{-2}.d^{-1}$ (Table 3.3). At Figure Eight Lake, [SRP] and $[Fe^{2+}]$ in anaerobic lakewater were greater than in porewater (Table 3.2 and 3.3).

Average water content (POR) in the shallow sediments varied from 28% at Jenkins to 89% at Figure Eight Lake. Generally, particulate P fractions were lowest at Narrow Lake and highest at Figure Eight Lake. In the study lakes, ORG-P varied most, over 26-fold; NaOH-P, CDB-P and HCl-P varied 14-, 6-, and 3-fold, respectively (Table 3.4). Most sediment P was in the CDB-P, HCl-P and ORG-P fractions; relatively little was present in the NaOH-P fraction (Table 3.4). HCl-P was highest at Minnie Lake. At Minnie Lake, apatite precipitation or adsorption of P onto Ca (possible at high porewater pH) may have enriched the sediments in HCl-P.

In the shallow sediments of this study, average sediment P fractions were almost always lower than those in hypereutrophic prairie lakes in southern Saskatchewan and Manitoba (Allan et al., 1980; Table 3.4). However, HCl-P was higher at Minnie and S-9 lakes than in the Saskatchewan and Manitoba lakes (Table 3.4). The relative amount of P in NAIP, which contains the maximum available P, was similar in both studies. The relative amount of ORG-P was lower and of HCL-P was higher in my lakes than in the prairie lakes studied by Allan et al. (1980; Fig. 3.2). Generally, total P content or exchangeable P fractions increase with lake depth, whereas HCl-P concentrations are highest nearshore and decrease with depth (Frink, 1969; Williams et al., 1976; Schindler et al., 1977; Skogheim, 1978; Ulen, 1978; Jacoby et al., 1982;

Psenner and Pucksko, 1988). The differences between P fractions in my sediments and those sampled by Allan et al. (1980) may be due to the sample location within the lake, but may also be due the difference in trophic status between the lakes. In general, my lakes were eutrophic and sediments were collected from one to four shallow depths (from 0.5- to 10-m depth), whereas their lakes were hypereutrophic and sediments were only collected near the deepest site (from 1- to 21-m depth).

Correlations between sediment and lakewater parameters

Lakewater pH and [SRP] just above the sediments were highly correlated with porewater pH and [SRP] in the top 10 cm of the sediment (r = 0.51 and 0.90, respectively; Table 3.5). This indicates there may be release of P from sediments to lakewater. In addition, potential P release from sediments by molecular diffusion was correlated with three of the four sediment P fractions (CDB-P, NaOH-P and ORG-P; $P < 0.01$; Table 3.5). The results from this in-situ study suggest that the magnitude of the particulate P fractions may be related to potential P release from shallow sediments. Similar relationships between particulate P fractions and P release from sediments have been reported in laboratory studies (Hosomi et al., 1981; Messer et al., 1984; Nurnberg, 1988).

Correlations between lakewater and porewater [SRP] and between potential sediment P release by molecular diffusion and CDB-P or NaOH-P suggest that sediments interact with [SRP] in lakewater, and may regulate P release from sediments. However, movement of anaerobic porewater into aerobic lakewater would result in oxidation of Fe^{2+}, which could lead to P sorption onto Fe^{3+}-complexes (e.g., Mortimer, 1941). Penetration of dissolved oxygen into sediments is confined to

the upper few mm (Klapwijk and Snodgrass, 1984; Carlton and Wetzel, 1988). In aerobic water, most P adsorbed onto Fe when Fe:P molar ratios were greater than 1.8; at molar ratios less than 1.8, some Fe-P sorption may occur (Tessenow, 1974). At 21 of 27 sampled sites, Fe:P molar ratios in porewater were less than 1.8 (Table 3.2). Thus, P could be released from anaerobic porewater into aerobic lakewater at most sites. However, [SRP] in lakewater above the sediment-water interface was negatively correlated with the Fe:P molar ratio in porewater (r = 0.65; Table 3.5). This indicates that the amount of Fe relative to P in porewater may limit P release from sediments to lakewater. Adsorption onto particulate sediments in the top few mm (aerobic porewater) may further limit P release from sediments. Since mixing in the upper few mm of shallow sediments is intense (Carignan and Tessier, 1985), adsorption of porewater P onto particulate sediments may not prevent exchange of P between porewater and lakewater. However, Fe-P sorption in aerobic porewater and onto particulate sediments may partly explain the poor correlations between porewater and lakewater parameters; porewater [SRP] and RATIO explained less than 50% of the lakewater [SRP] variance between the sites.

Correlations between porewater and particulate sediment parameters

In porewater, [SRP] and [Fe^{2+}] were positively correlated regardless if Figure Eight Lake data were included or excluded (Table 3.6). The relationship between porewater [SRP] and [Fe^{2+}] is similar to relationships found at two hypereutrophic lakes in Indiana (Theis and McCabe, 1978). Porewater [SRP] and pH were correlated when data from Figure Eight Lake were excluded (Table 3.5). The correlation between porewater [SRP] and pH may indicate competition of phosphate with

hydroxide ions for adsorption sites on iron oxy-hydroxides (Lijklema, 1977).

Most correlations between water content and particulate P fractions were highly significant (r = 0.42-0.84; $P < 0.01$), except for the relationship between ORG-P and HCl-P (Table 3.6). Again, correlation coefficients were affected little regardless whether data from Figure Eight were included or excluded. Other studies have reported similar relationships between P fractions in both shallow sediments and deep sediments (Williams et al., 1971a,b, 1976; Wildung et al., 1977; Skogheim, 1978; Ostrofsky, 1987).

Correlations between porewater pH and particulate sediment parameters are all significant, except for the correlation between porewater pH and HCl-P (Table 3.6). Porewater [Fe^{2+}] was related to NaOH-P and HCl-P. Porewater [SRP] was only correlated to NaOH-P; however, this relationship was not significant when data from Figure Eight Lake were excluded. Little of the variance of porewater and particulate sediment parameters was explained by the correlations; this is similar to relationships found at Monroe Lake, a shallow lake in Florida flushed by a river (Ali et al., 1988). In addition, a multiple regression of NaOH-P or CDB-P and pH on porewater [SRP] did not explain more variance than the single significant relationship between porewater pH and [SRP] (multiple regression: r = 0.24 or 0.25, respectively, $P < 0.05$; single regression: r = 0.24, $P < 0.01$). Reduction of the within-site variability did not improve the previously discussed correlations (Table 3.7).

The lack of strong correlations between porewater and particulate sediment parameters may indicate: (1) the extraction procedure does not

isolate the particulate P fraction that controls P exchange with porewater, and/or (2) adsorption/desorption of P from particulate sediment fractions is not a simple equilibration reaction between P in porewater and in particulate sediments. This result is unlike a previously reported relationship between NaOH-P and porewater SRP in an Austrian lake (Psenner, 1984). However, his extraction method differed from this study and his sediments were only from one lake. In my study, sediments were collected from lakes in various hydrological watersheds, which had different geochemical conditions (e.g., sulfur bacteria in Minnie Lake). Low correlations between particulate P fractions and potential P release from sediments in my study may also indicate differences in sediment locations, depths, sampling times and diversity of the lakes (Nurnberg, 1988).

Redox potential, pH, Fe, Ca, S, organic material and biological activity may influence the partitioning of P in sediments. These factors may differ between lakes, which may have resulted in low simple correlation coefficients between particulate P fractions and porewater [SRP]. Although redox potential was not measured in this study, redox potential may not differ greatly between sites; penetration of oxygen from aerobic lakewater into sediments is small, in the order of 1 to 4 mm (Klapwijk and Snodgrass, 1984; Carlton and Wetzel, 1988). If penetration of oxygen into sediments is only a few mm, then (1) all porewater was essentially anaerobic, and (2) redox potential would not affect the variation of P in porewater and particulate sediments observed in the study lakes.

3.5 CONCLUSIONS

This study of the relationships between P in lakewater, porewater and particulate sediments in shallow sites of lakes in central Alberta indicates that:

(1) Lakewater [SRP] were positively correlated to [SRP] and molar ratio of Fe:P (RATIO) in porewater; however, porewater [SRP] or RATIO explained little variation in lakewater [SRP].

(2) Potential P release by molecular diffusion was positively correlated with CDB-P and NaOH-P.

(3) Porewater [SRP], $[Fe^{2+}]$ and pH were positively correlated with one another.

(4) P fractions in particulate sediments were highly correlated with one another.

(5) P in particulate fractions and porewater were not correlated.

(6) Sediment P dynamics are complex and cannot be described by simple correlations. A multivariate analyses of a data set (which includes Ca, S and alkalinity in porewater and Ca and Fe in particulate sediments) may provide further insight into the potential factors regulating porewater [SRP], and rates of P release from sediments.

3.6 REFERENCES

Adams, D. D., G. Matisoff, and W. J. Snodgrass. 1982. Flux of reduced chemical constituents (Fe^{2+}, Mn^{2+}, NH_4^+, and CH_4) and sediment oxygen demand in Lake Erie. Hydrobiologia 92:405-414.

Alberta Environment. 1986. Minnie Lake stabilization study. Summary report. Planning Division, Alberta Environment, Edmonton, Ab. 69p.

Ali, A., K. R. Reddy, and W. F. DeBusk. 1988. Seasonal changes in sediment and water chemistry of a subtropical shallow eutrophic lake. Hydrobiologia 159:159-167.

Allan, R. J., J. D. H. Williams, S. R. Joshi, and W. F. Warwick. 1980. Historical changes and relationship to internal loading of sediment phosphorus forms in hypertrophic prairie lakes. J. Environ. Qual. 9:199-206.

American Public Health Association. 1985. Standard methods for the examination of water and wastewater. 5th ed. APHA, AWWA, WPCF. New York. 1143 p.

Andersen, J. M. 1975. Influence of pH on release of phosphorus from lake sediments. Arch. Hydrobiol. 76:411-419.

Berner, R. A. 1980. Early diagenesis. Princeton University Press, NJ. 241 p.

Bray, J. T., O. P. Bricker, and B. N. Troup. 1973. Phosphate in interstitial waters of anoxic sediments: Oxidation effects during sampling procedure. Science. 180:1362-1364.

Carignan, R. 1984a. Interstitial water sampling by dialysis: methodological notes. Limnol. Oceanogr. 29:667-670.

Carignan, R. 1984b. Sediment geochemistry in a eutrophic lake colonized

by the submersed macrophyte Myriophyllum spicatum. Verh. Internat. Verein. Limnol. 22:355-370.

Carignan, R. and A. Tessier. 1985. Zinc deposition in acid lakes: the role of diffusion. Science 228:1524-1526.

Carlton, R. G., and R. G. Wetzel. 1988. Phosphorus flux from lake sediments: effect of epipelic algal oxygen production. Limnol. Oceanogr. 33:562-570.

Carritt, D. E., and S. Goodgal. 1954. Sorption reactions and some ecological implications. Deep-Sea Res. 4:224-243.

Dixon, W. J. 1983. BMDP Statistical Software. Univ. of California Press. Berkely, CA. 734p.

Frink, C. R. 1969. Chemical and mineralogical characteristics of eutrophic lake sediments. Soil Sci. Soc. Amer. Proc. 33:369-372.

Golterman, H. L. 1984. Sediments, modifying and equilibrating factors in the chemistry of freshwater. Verh. Internat. Verein. Limnol. 22:23-59.

Green, R. 1972. Geological map of Alberta Research Council of Alberta. Map (scale 1:1,267,000). Edmonton, Ab.

Hesslein, R. H. 1976. An in situ sampler for close interval pore water studies. Limnol. Oceanogr. 21:912-914.

Holdren, G. C., and D. E. Armstrong. 1980. Factors affecting phosphorus release from intact sediment cores. Environ. Sci. Technol. 14:79-87.

Holdren, G. C., Jr., D. E. Armstrong, and R. F. Harris. 1977. Interstitial inorganic phosphorus concentrations in Lakes Mendota and Wingra. Water Res. 11:1041-1047.

Hosomi, M., M. Okada, and R. Sudo. 1981. Release of phosphorus from

sediments. Verh. Internat. Verein. Limnol. 21:628-633.

Jacoby, J. M., D. D. Lynch, E. B. Welch, and M. A. Perkins. 1982. Internal phosphorus loading in a shallow eutrophic lake. Water Res. 16:911-919.

Kamp-Nielsen, L. 1975. A kinetic approach to the aerobic sediment-water exchange of phosphorus in Lake Esrom. Ecol. Model. 1:153-160.

Kjearsgaard, A. A. 1972. Reconnaissance soil survey of the Tawatinaw map sheet (83-I). Alberta Institute of Pedology. Report No. S-72-29. Edmonton, Ab. 103p.

Klapwijk, A., and W. J. Snodgrass. 1986. Lake oxygen model 3: Simulation of ammonia, nitrate, and oxygen in Hamilton Harbour (1977-1978). p. 265-288. In P. G. Sly (ed.). Sediments and Water Interactions (Proc. 3rd Symp. on Interactions between sediments and water). Spinger-Verlag, New York, NY. 521 p.

Lijklema, L. 1977. The role of iron in the exchange of phosphate between water and sediments. p 313-317. In H. L. Golterman (ed.). Interactions between sediments and freshwater. (Proc. S.I.L.-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands.

Logan, T. J., T. O. Oloya, and S. M. Yaksich. 1979. Phosphate characteristics and bioavailability of suspended sediments from streams draining into Lake Erie. J. Great Lakes Res. 5:112-123.

Mawhinney, M. R., and C. Bisutti. 1987. Common corers and grab samplers operating manual. (Available through Technical Operations). NWRI, Burlington, Ont. 33p.

Mayer, T., and J. D. H. Williams. 1981. Modified procedure for determining the forms of phosphorus in freshwater sediments. Technical Bulletin No. 119. Environment Canada, Burlington,

Ontario. 11p.

Messer, J. J., J. M. Ihnat, and D. L. Wegner. 1984. Phosphorus release from the sediments of Flaming Gorge Reservoir, Wyoming, U.S.A. Verh. Internat. Verein. Limnol. 22:1457-1464.

Moran, S. R., A. E. Howard, and M. R. Trudell. 1986. Groundwater-induced soil salinization around pothole sloughs in east-central Alberta. In Proc. Internat. Assoc. Hydrogeologists, 3rd Canadian Hydrogeological Conference, April 20-23, 1986. Saskatoon, Saskatchewan.

Mortimer, C. H. 1941. The exchange of dissolved substances between mud and water in lakes. J. Ecol. 29:280-329.

Murphy, J., and J. P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27:31-36.

Nurnberg, G. K. 1988. Prediction of phosphorus release rates from total and reductant-soluble phosphorus in anoxic lake sediments. Can J. Fish. Aquat. Sci. 45: 453-462.

Ostrofsky, M. 1987. Phosphorus species in the surficial sediments of lakes of eastern North America. Can. J. Fish. Aquat. Sci. 44:960-966.

Pfennig, N. 1978. General physiology and ecology nof photosynthetic bacteria. p. 3-18. In R. K. Clayton and W. R. Sistrom (eds.). The Photosynthetic Bacteria. Plenum Press, New York. 946 p.

Prepas, E. E., and T. Murphy. 1987. Report on the 1986 treatment of Figure 8 Lake. Planning Division, Alberta Environment. Edmonton, Ab. 105p.

Prepas, E. E., M. E. Dunnigan, and A. M. Trimbee. 1988. Comparison of in

situ estimates of chlorophyll *a* obtained with Whatman GF/F and GF/C glass-fiber filters in mesotrophic to hypereutrophic lakes. Can. J. Fish. Aquat. Sci. 44: 910-914.

Psenner, R. 1984. Phosphorus release patterns from sediments of a meromictic mesotrophic lake (Piburger See, Austria). Verh. Internat. Verein. Limnol. 22:219-228.

Psenner, R., and R. Pucsko. 1988. Phosphorus fractionation: advantages and limits of the method for the study of sediment P origins and interactions. Arch. Hydrobiol. Beih. 30:43-59.

Quigley, M. A., and J. A. Robbins. 1986. Phosphorus release processes in nearshore southern Lake Michigan. Can. J. Fish. Aquat. Sci. 43:1201-1207.

Ripl, W., and G. Lindmark. 1979. The impact of algae and nutrient composition on sediment-exchange dynamics. Arch. Hydrobiol. 86:45-65.

Schindler, D. W., R. Hesslein, and G. Kipphut. 1977. Interactions between sediments and overlying waters in natural oligotrophic and experimentally eutrophied Precambrian Shield lakes. p. 235-243. In H. L. Golterman (ed.). Interactions between sediments and freshwater. (Proc. S.I.L.-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands.

Skogheim, O. K. 1978. Recent sediments in a eutrophic lake: Arungen, Norway. Verh. Internat. Verein. Limnol. 20:749-757.

Sokal, R. R., and F. J. Rohlf. 1981. Biometry. 2nd ed. Freeman, San Francisco, CA.

Stauffer, R. E., and D. E. Armstrong. 1984. Lake mixing and its relationship to epilimnetic phosphorus in Shagawa Lake, Minnesota.

Can. J. Fish. Aquat. Sci. 41:57-69.

Strong, W. L., and K. R. Leggat. 1981. Ecoregions of Alberta. Alberta Energy and Natural Resources, ENR Technical Rep., No. T/41, Edmonton, Ab. 64p.

Syers, J. K., R. F. Harris, and D. E. Armstrong. 1973. Phosphate chemistry in lake sediments. J. Environ. Qual. 2:1-14.

Tessenow, U. 1972. Losungs-, Diffusions- and Sorptions-Prozesse in der Oberschicht von Seesedimenten. Part 1. Arch. Hydrobiol. Suppl. 38:353-398.

Tessenow, U. 1974. Losungs-, Diffusions- and Sorptions-Prozesse in der Oberschicht von Seesedimenten. Part 3. Arch. Hydrobiol. Suppl. 47:1-79.

Theis, T. L., and P. J. McCabe. 1978. Phosphorus dynamics in hypereutrophic lake sediments. Water Res. 12:677-685.

Trew, D. O., D. J. Beliveau, and E. I. Yonge. 1987. The Baptiste Lake study. Technical Report. Water Quality Control Branch, Pollution Control Division, Alberta Environment, Edmonton, Ab. 380p.

Trew, D. O., E. I. Yonge, and R. P. Kaminski. 1981. A preliminary trophic assessment of nine lakes in the Cold Lake region. Water Quality Control Branch, Pollution Control Division, Alberta Environment, Edmonton, Ab. 70p.

Troup, B. N., O. P. Bricker, and J. T. Bray. 1974. Oxidation effect on the analysis of iron in the interstitial water of recent anoxic sediments. Nature 249:237-239.

Truper, H. G., and N. Pfennig. 1978. Taxonomy of the Rhodospirillales. p. 19-27. In R. K. Clayton and W. R. Sistrom (eds.). The Photosynthetic Bacteria. Plenum Press, New York. 946 p.

Ulen, B. 1978. Seston and sediment in Lake Norrviken. 3. Nutrient release from sediment. Schweiz. Z. Hydrol. 40:287-305.

Van Eck, G. Th. M., and H. G. C. Smits. 1986. Calculation of nutrient fluxes across the sediment-water interface in shallow lakes. p. 289-301. In P. G. Sly (ed.). Sediments and Water Interactions (Proc. 3rd Symp. on Interactions between sediments and water). Spinger-Verlag, New York, NY. 521 p.

Vollenweider, R. A. 1968. Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorus as factors in eutrophication. OECD Report DAS/CSI/68-27. Organization for Economic Co-operation and Development, Directorate for Scientific Affairs, Paris.

Wetzel, R. G. 1983. Limnology. 2nd ed. Saunders, Philadelphia, PA. 767p.

Wildung, R. E., R. L. Schmidt, and R. C. Routson. 1977. The phosphorus status of eutrophic lake sediments as related to changes in limnological conditions - phosphorus mineral components. J. Environ. Qual. 6:100-104.

Williams, J. D. H., J.-M. Jaquet, and R. L. Thomas. 1976. Forms of phosphorus in the surficial sediments of Lake Erie. J. Fish. Res. Board Can. 33:413-429.

Williams, J. D. H., J. K. Syers, D. E. Armstrong, and R. F. Harris. 1971a. Characterization of inorganic phosphate in noncalcareous lake sediments. Soil Sci. Soc. Amer. Proc. 35:556-561.

Williams, J. D. H., J. K. Syers, S. S. Shukla, R. F. Harris, and D. E. Armstrong. 1971b. Levels of inorganic and total phosphorus in lake sediments as related to other sediment parameters. Environ. Sci. Technol. 5:1113-1120.

Table 3.1. Summer thermal regime (S=stratified, M=mixed), surface and drainage basin area (A_o and A_d, respectively), maximum depth (z_{max}), mean summer concentration of total phosphorus (TP) and chlorophyll *a* (Chl*a*), alkalinity (Alk) and Ca in the trophogenic zone of nine Alberta lakes. Blanks indicate no data available.

Lake	Mixing regime	A_o	A_d	z_{max}	TP	Chl*a*	Alk ($CaCO_3$)	Ca
		km^2		m	$mg.m^{-3}$		$g.m^{-3}$	
Baptiste[1,2]	S	4.6	179	26	38	24	162	35
Figure Eight[3]	M	0.4	4	6	250	172	91	26
Island[1,2]	S	1.0	7	15	20	5	199	26
Jenkins[4]	S	1.8	101	18	25	42	134	27
Long[4]	S	1.6	23	28	13	4	161	38
Minnie[5]	S	0.8	.5	24	34	6	338	19
Narrow[4]	S	1.1	7	36	11	3	156	35
S-9[6]	M	0.03	0.3	2.5	46			
Tucker[2,7]	M	7.2	150	7	42	23	200	26

References: 1 Trew et al., 1987; 2 Monitoring Branch, Alberta Environment, unpubl. data; 3 Prepas and Murphy, 1987; 4 Prepas et al., 1988; 5 D. O. Trew, Alberta Environment, pers. comm.; 6 this study; 7 Trew et al., 1981.

Table 3.2. Concentrations (x (SE)) of soluble reactive phosphorus (SRP) and ferrous iron (Fe^{2+}), and pH in porewater from the top 10 cm of bottom sediments from nine Alberta lakes. Average molar ratio of Fe^{2+}:SRP in porewater (RATIO), depths of the sampled sites and number of samples per lake (n) are also indicated.

Lake Depth (m)	n	SRP $mg.m^{-3}$	Fe^{2+} $mg.m^{-3}$	pH[1]	RATIO
Baptiste 2.5,5	9	456 (65)	255 (36)	7.9	0.7 (0.1)
Figure Eight 5	5	3622 (189)	1010 (94)	7.8	0.3 (0.0)
Island 2.5,4,5,7.5	20	282 (56)	232 (8)	8.0	1.4 (0.2)
Jenkins 4,5,7.5	13	1960 (157)	360 (36)	8.0	0.2 (0.0)
Long 2.5,4,5	15	249 (37)	942 (229)	7.9	4.4 (1.0)
Minnie 5,7.5	10	1009 (201)	977 (146)	9.5	1.2 (0.2)
Narrow 2.5,5,7.5,10	20	68 (10)	250 (57)	7.8	3.7 (0.5)
S-9 0.5,1,1,3	20	415 (115)	702 (110)	7.7	7.9 (3.2)
Tucker 2.5,4,5,7	14	356 (75)	166 (16)	9.0	0.6 (0.1)

[1] SE of pH was within 0.1 units of the mean.

Table 3.3. Concentrations (x (SE)) of SRP, Fe^{2+} and pH in lakewater just above the bottom sediments in nine Alberta lakes. Ranges of SRP gradients across the sediment-water interface and potential release rates of SRP from sediments to lakewater by molecular diffusion (PFLUX) are also indicated. Depths and abbreviations as indicated in Table 3.2.

Lake	SRP	Fe2+	pH	SRP gradient	P flux
	$mg.m^{-3}$			$mg.m^{-4}$	$mg.m^{-2}.d^{-1}$
Baptiste	19 (6)	58 (11)	8.1	6500 - 9200	0.17 - 0.47
Figure Eight	4675 -	1768 -	7.3	-19100	-
Island	9 (4)	44 (10)	8.0	2300 - 9500	0.02 - 0.33
Jenkins	43 (13)	68 (19)	8.2	32600 - 40600	0.35 - 0.62
Long	4 (2)	51 (16)	8.2	2300 - 6200	0.22 - 0.49
Minnie	29 (22)	93 (7)	9.3	8000 - 27700	0.67 - 2.31
Narrow	6 (0)	38 (9)	8.0	400 - 2100	0.01 - 0.06
S-9	13 (3)	100 (26)	8.0	500 - 20400	0.01 - 0.52
Tucker	44 (15)	120 (57)	9.2	2400 - 11700	0.15 - 0.22

Table 3.4. Water content (by weight, POR) and phosphorus fractions in the top 10 cm of bottom sediments (x (SE)) from nine Alberta lakes and the mean sediment P fractions from eight other prairie lakes (Other; Allan et al., 1980). Depths as indicated in Table 3.2.

Lake	POR	CDB-P	NaOH-P	HCl-P	ORG-P
	%	in ug.g^{-1} dry weight			
Baptiste	52 (6)	86 (6)	14 (2)	152 (10)	131 (49)
Figure Eight	89 (1)	409 (121)	110 (4)	129 (4)	261 (30)
Island	42 (7)	132 (48)	15 (4)	174 (26)	92 (29)
Jenkins	28 (4)	121 (16)	8 (1)	191 (29)	18 (5)
Long	87 (2)	300 (46)	30 (2)	210 (11)	231 (21)
Minnie	85 (2)	232 (22)	24 (2)	405 (14)	125 (23)
Narrow	44 (3)	73 (7)	8 (1)	139 (8)	41 (3)
S-9	34 (1)	96 (6)	12 (1)	359 (5)	10 (1)
Tucker	64 (8)	351 (64)	21 (4)	194 (27)	139 (27)
Other	-	528 (99)[1]	-	249 (15)	444 (42)

[1] combined NaOH-P and CDB-P fractions

Table 3.5. Product-moment correlation coefficients between average sediment (porewater (PW) and particulate) and lakewater parameters in eight meso-eutrophic to eutrophic lakes. Significance level indicated as $^{*}P < 0.05$, $^{**}P < 0.01$, $^{***}P < 0.001$ (df = 24).

	Lakewater			
	SRP	Fe2+	pH	PFLUX
PW SRP	0.51**	0.34	0.20	0.81***
Fe2+	-0.19	0.34	-0.12	0.40*
pH	-0.42*	0.18	0.90***	0.46*
RATIO	-0.65***	-0.12	-0.28	-0.55**
POR	0.06	-0.11	0.36	0.49*
CDB-P	0.37	-0.05	0.37	0.56**
NaOH-P	0.16	-0.14	0.22	0.50**
HCl-P	0.28	0.18	0.14	0.36
ORG-P	0.04	-0.24	0.26	0.43*

Table 3.6. Matrix of product-moment correlation coefficients between transformed porewater and particulate sediment parameters in the nine study lakes (lower left corner, df = 119) and in eight eutrophic lakes (minus Figure Eight Lake data; upper right corner, df = 124). Significance indicated as in Table 3.5.

	SRP	Fe^{2+}	pH	POR	CDB-P	NaOH-P	HCl-P	ORG-P	RATIO
SRP		0.47***	0.17	0.02	0.11	0.18*	0.05	-0.06	
Fe^{2+}	0.41***		-0.04	0.19*	0.17	0.39***	0.35***	-0.02	
pH	0.24*	<0.01		0.40***	0.33***	0.15	0.18*	0.25**	0.21*
POR	-0.09	0.13	0.45***		0.84***	0.83***	0.36***	0.84***	0.10
CDB-P	0.01	0.11	0.39***	0.84***		0.81***	0.51***	0.63***	0.00
NaOH-P	0.01	0.32***	0.25**	0.83***	0.82***		0.42***	0.67***	0.07
HCl-P	0.11	0.40***	0.17	0.43***	0.58***	0.56***		0.04	0.19*
ORG-P	-0.16	-0.08	0.29**	0.83***	0.61***	0.65***	0.08		0.05
RATIO			-0.25**	0.18*	0.06	0.21*	0.16	0.12	

Table 3.7. Product-moment correlation coefficients between average porewater and particulate sediment parameters in the nine study lakes (lower left corner, df = 25) and in eight eutrophic lakes (minus Figure Eight Lake data; upper right corner, df = 24). Significance indicated as in Table 3.5.

	Porewater (PW)							
	SRP	Fe^{2+}	pH	POR	CDB-P	NaOH-P	HCl-P	ORG-P
PW SRP		0.43*	0.15	0.03	0.16	0.19	0.02	0.02
PW FE^{2+}	0.36		-0.11	0.15	0.13	0.38	0.34	-0.04
PW pH	0.23	-0.06		0.46*	0.42*	0.21	0.24	0.33
POR	-0.09	0.09	0.53**		0.89***	0.85***	0.41*	0.86***
CDB-P	0.07	0.07	0.48*	0.88***		0.85***	0.55**	0.72***
NaOH-P	0.01	0.30	0.34	0.86***	0.86***		0.44*	0.71***
HCl-P	0.09	0.40*	0.22	0.47*	0.62***	0.60**		0.11
ORG-P	-0.08	-0.11	0.39*	0.85***	0.70***	0.70***	0.16	

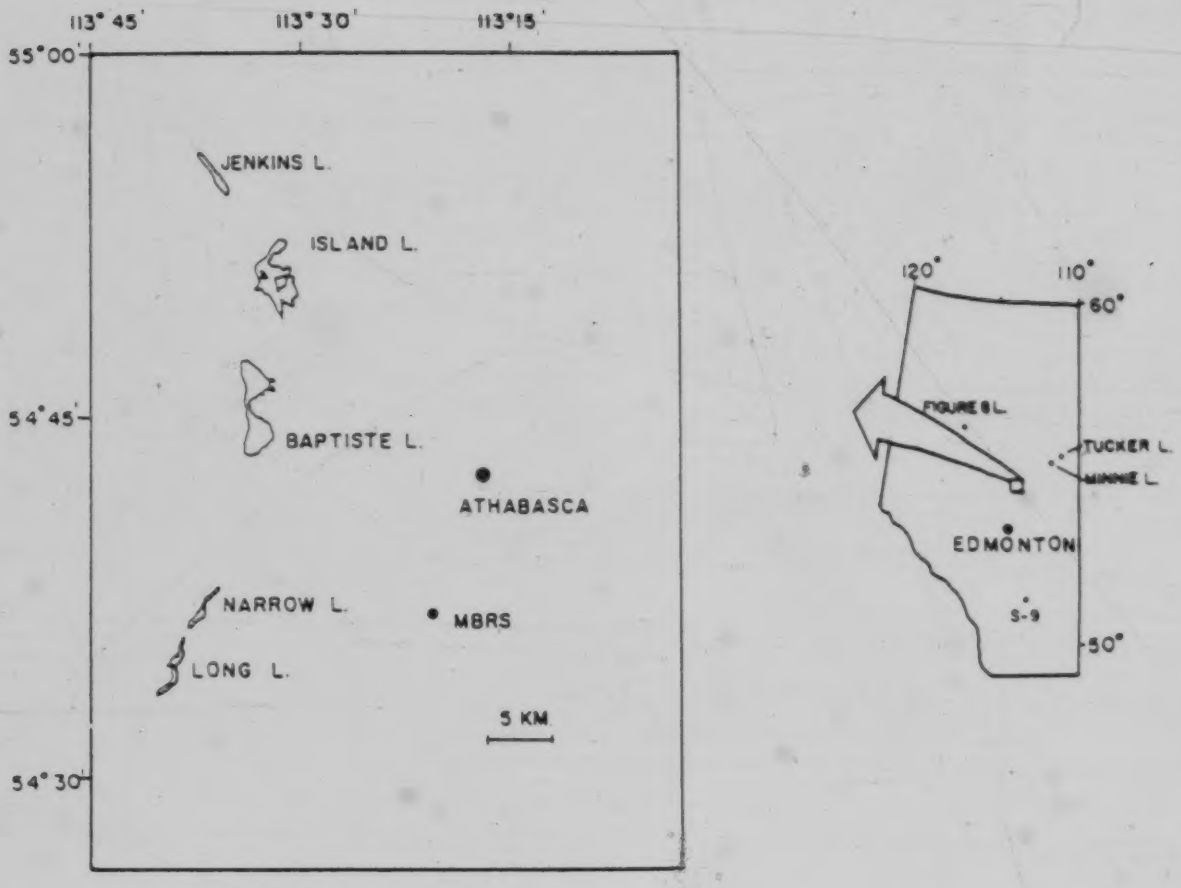


Figure 3.1. Location of study lakes.

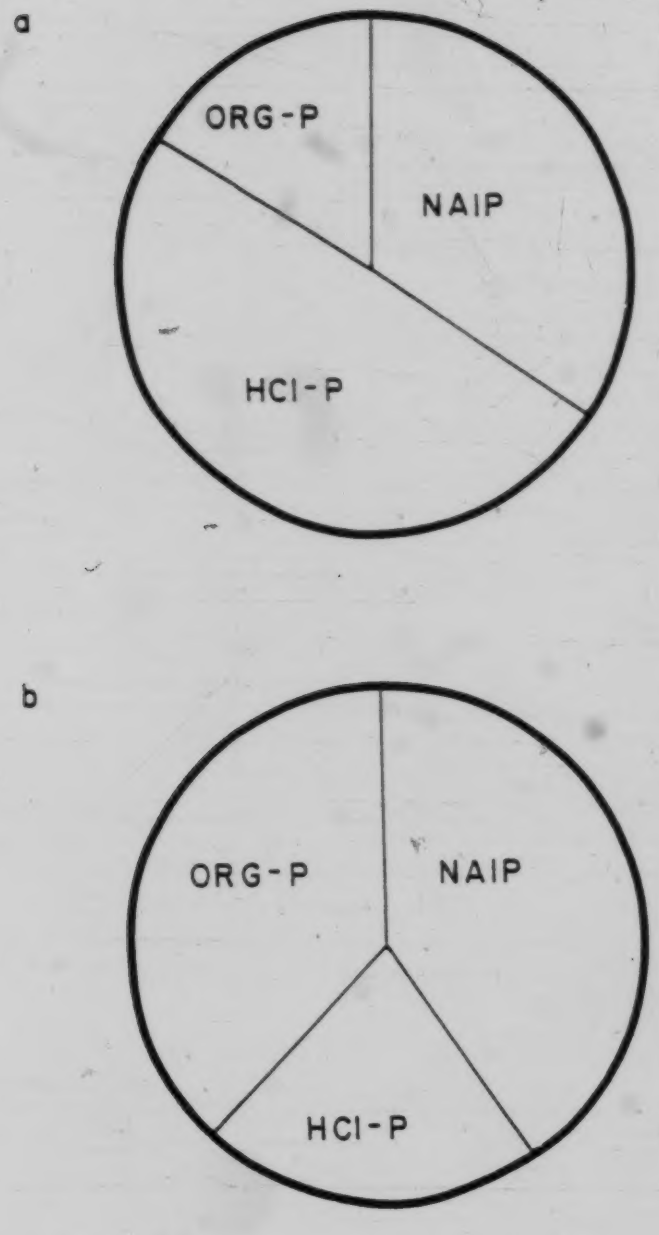


Figure 3.2. Mean contribution of three sediment phosphorus (P) fractions (NAIP, HCl-P and ORG-P) to total P in shallow sediments in (a) this study and (b) Allan et al. (1980).

4. RELATIONSHIPS BETWEEN PHOSPHORUS IN SHALLOW SEDIMENTS AND IN THE TROPHOGENIC ZONE OF SEVEN ALBERTA LAKES[1]

4.1 ABSTRACT

Relationships between phosphorus (P) in bottom sediments, soluble reactive P in lakewater just above the sediment (LWP), and total P in the trophogenic zone (TZP) were investigated in seven meso-eutrophic to eutrophic Alberta lakes in 1986. Sediments, porewater and overlying water were collected from two to four shallow sites within the trophogenic zone ($\leq$ 10-m depth) at each lake. The amount of P in particulate sediments or porewater was not correlated with TZP ($P > 0.05$). LWP was positively correlated with TZP ($r = 0.86$, $P < 0.05$). Principal component analyses of porewater and particulate sediment parameters resulted in two principal components (PC), which separated the study lakes from each other. Average factor scores of the second PC (a mobile porewater P component) were correlated with LWP ($r = 0.75$, $P < 0.001$) and TZP ($r = 0.77$, $P < 0.05$). This study indicates that P in shallow sediments may be an important source of P to the trophogenic zone.

[1]A version of this chapter has been submitted for publication. J.F.H. Shaw and E.E. Prepas. Water Research.

4.2 INTRODUCTION

Lake bottom sediments contain a vast pool of phosphorus (P); e.g., the amount of P in sediments may be comparable to that present in the entire water column of shallow lakes. Since P is generally the nutrient limiting algal production in freshwater lakes, P release from sediments could affect lakewater quality. Most P in sediments is bound to particulate matter. Although this particulate P is generally not mobile, it can be solubilized into porewater. Diffusion, groundwater, mixing and bioturbation may transport P from porewater into lakewater (Bostrom et al., 1982).

P release from sediments into anaerobic lakewater is generally greater than into aerobic lakewater. However, P released from hypolimnetic sediments into anaerobic lakewater does not reach the trophogenic zone until the thermocline is depressed during overturn or storms (Stauffer and Armstrong, 1984). Generally, the amount of P in deep (hypolimnetic) sediments is not correlated with P concentrations present in surface water (e.g., Ohle, 1964; Hakanson, 1984; Ostrofsky, 1987). In contrast to hypolimnetic sediments, P released from shallow sediments into aerobic lakewater enters surface waters directly. Thus, P release from shallow sediments may have a much greater impact on surface waters than P release from hypolimnetic sediments. Although the extent of shallow sediments has been correlated with P concentrations in surface water (Fee, 1979), I am not aware of other studies comparing chemistry of shallow sediments to P concentration in the trophogenic zone. The objective of this study was to examine relationships between characteristics of shallow sediments (porewater and particulate

sediments) and P concentration in lakewater above these sediments and in the trophogenic zone.

4.3 MATERIAL AND METHODS

Study lakes

The study lakes (Table 4.1) are situated on sedimentary bedrock; glacial till is the primary surficial deposit (Green, 1972; Kjearsgaard, 1972). All lakes are in the mixed-wood section of the boreal forest (Strong and Leggat, 1981). There is recreational development (camps and cottages) around all lakes except Tucker Lake, and moderate agricultural activity in the drainage basins of all lakes, except Long, Narrow and Tucker lakes. The entire water column in one of the lakes (Tucker) mixed intermittently during summer, and one lake (Minnie) was more saline than the others. Morphometry, conductivity, total P and dissolved P concentrations varied between lakes (Table 4.1). Based on mean summer total P concentrations in the trophogenic zone (TZP; Wetzel, 1983), trophic status of all lakes varied from meso-eutrophic to eutrophic (Table 4.1).

Sampling design

Shallow sites in the trophogenic or epilimnetic zone (whichever extended deeper into the water column; after Hutchinson, 1959) were sampled from May to August. During this period, I collected porewater, lakewater just above the sediment-water interface and sediments from two to four sites per lake (Table 4.2); the sites were on a transect perpendicular to shore. The location of the transect was selected to represent average lake slope (i.e., ratio of distance from shore and

lake depth). At each site, porewater and particulate sediments were collected from the top 10 cm of the sediment; exchange of P between these sediments and lakewater can occur (Tessenow, 1972).

Water collection and analyses

Sediment porewater and water overlying sediments were collected with parallel dialysis chambers (peepers), fitted with Gelman HT-450 membrane filters (Hesslein, 1976; Carignan, 1984; Chapter 2). At each site, duplicate peepers were placed in the sediment by SCUBA divers. Water from peeper chambers was retrieved after two weeks and stored as outlined in Chapter 3. The following samples were collected: (1) one lakewater sample pooled from 10 chambers above the sediment-water interface and (2) five porewater samples from 0 to 10 cm in the sediment at 2-cm intervals. Aliquots from these pooled samples were diluted 5 to 50 times with double distilled water (DDW).

Water from one half of each peeper was analyzed for soluble reactive P (SRP; Murphy and Riley, 1962); average SRP concentrations from both peepers at each site were used in subsequent data analyses. Water from the other half of the peepers was analyzed for ferrous iron (Fe^{2+}; APHA, 1981) and pH. Iron and pH are known to affect P release from sediments to lakewater (e.g., Tessenow, 1974; Lijklema, 1977). The preparation of samples, number of replicates and analyses were as described in Chapter 3.

Sediment collection and analyses

Particulate sediments from five lakes were collected with polyethylene core tubes (inner diameter = 6.5 cm) by SCUBA divers during the summer of 1986. Sediments from the other two lakes (Baptiste and

Minnie) were collected with a benthos gravity corer during April 1987 (Mawhinney and Bisutti, 1987). In most cases, three cores were retrieved from each site; these were sectioned in the field at 2-cm intervals, to a depth of 10 cm. Only the top 6 cm of a core was obtained from Tucker Lake. All sections were frozen until they could be analyzed.

Water content (POR) was determined on all sections of sediments. Sediments were dried at 60 ^{o}C for 2 d to reach constant weight. To reduce the number of sediment P analyses, sections from only one core per site were analyzed. Each section of this one core was ground with mortar and pestle. The ground sediments (<150 um) were analyzed in duplicate for CDB-P, NaOH-P, HCl-P and ORG-P (Mayer and Williams, 1981). NaOH-P and CDB-P represent fractions that most likely exchange P with porewater over short- and long-term periods, respectively; the combination of these fractions is considered the maximum potentially available P in sediments (Logan et al., 1979). P analyzed as HCl-P and ORG-P is bound to apatite-like complexes and refractory organic material, respectively; these two fractions generally do not exchange P with porewater (Sommers et al., 1972; Williams et al., 1980). Average values for POR and sediment P fractions from each site were used in subsequent data analyses. To combine particulate sediment and porewater data for each 2-cm section, I used porosity and particulate sediment data from Tucker Lake (the top 6 cm) for the top three sections.

Data analyses

Simple relationships between particulate sediment (CDB-P, NaOH-P, HCl-P, ORG-P, POR), porewater (SRP, Fe^{2+}, pH) and lakewater (SRP and Fe^{2+} just above the sediments) parameters, and mean summer total P

concentrations in the trophogenic zone (TZP) were evaluated by correlation. In addition, TZP was correlated with (1) rates of molecular diffusion of P from sediments to lakewater (FLUX; as calculated in Chapter 3; which was an estimate of the minimum P release from sediments), and (2) the molar ratio of Fe^{2+} to SRP in porewater, which could prevent P release from sediments (RATIO; Tessenow, 1974).

Several parameters may influence P exchange between particulate sediments and porewater, and between porewater and lakewater (Chapter 3); simple correlations may not adequately describe relationships between P in sediments and lake trophic status. Therefore, an examination of interrelationships between the measured parameters was carried out with a principal component analysis (PCA). Principal components (PC) are linear combinations of the original parameters, which maximally discriminate among each sample in the data set (Harris, 1979). PCA was performed with BMDP Statistical Software; a Varimax rotation was performed on those PC's with eigenvalues greater than 1 (Harris, 1975; Dixon, 1983).

Mean factor scores of PC's for each site or lake likely distinguish sites within a lake and the study lakes from each other. A PCA was performed to determine correlations between shallow sediment parameters and SRP concentrations in lakewater (LWP); all particulate P fractions, POR, RATIO, and FLUX were included as shallow sediment parameters. Porewater [SRP] and $[Fe^{2+}]$ were not included since they were used to calculate RATIO and FLUX. Average factor scores were calculated per site in each lake and correlated with LWP at these same sites. Average factor scores per lake were also correlated with TZP.

4.4 RESULTS AND DISCUSSION

Preliminary Data Evaluation

Characteristics of lakewater, porewater, and particulate sediments in the study lakes are presented in Tables 4.2 and 4.3, and have been described in detail and compared to other lakes in Chapter 3. In most study lakes, porewater [Fe^{2+}] increased slightly with sediment depth. CDB-P and ORG-P particulate fractions tended to increase with lake depth (e.g., Fig. 4.1). Water content was highest at deeper sites (e.g., Fig. 4.1), except at Long and Minnie lakes where POR was relatively high (> 74%) and constant with lake depth. No consistent patterns between other porewater and sediment parameters, and depth in the sediment or lake were found (e.g., Fig. 4.1).

Correlations were calculated with average lake values for each parameter, thus, reducing the variance of the original data set (i.e., variance caused by sampling different sediment and lake depths). Concentrations of several parameters varied greatly between lakes. To reduce the residual variance, all parameters were log-10 transformed, except POR, which was arcsine transformed (Sokal and Rohlf, 1981). These transformed data were assumed to have a multivariate normal distribution and equal dispersion (Green and Vascotto, 1978).

Porewater [Fe^{2+}] and [SRP] were higher than concentrations in lakewater just above the sediment-water interface (Table 4.2). Thus, diffusion of SRP and Fe^{2+} from porewater to lakewater may be possible. Potential release of P from sediments to lakewater by molecular diffusion (FLUX) ranged from 0.04 to 1.5 $mg.m^{-2}.d^{-1}$ (Table 4.2). Diffusion of P from anaerobic porewater to aerobic lakewater may be

prevented by P sorption onto ferric iron complexes, which form under aerobic conditions (e.g., Mortimer, 1941); oxygen penetration in porewater from oxygenated lakewater is limited to the upper few mm (Lijklema, 1977; Carlton and Wetzel, 1988). However, sorption of P into ferric iron complexes is not fully effective to prevent P release from sediment to lakewater when relatively little iron is present (i.e., molar ratio Fe:P < 1.8; Tessenow, 1974). At 19 of 22 sites in the seven study lakes, molar ratios of Fe^{2+} to SRP (RATIO) were less than 1.8; release of SRP from porewater to lakewater would not be prevented at these sites. At one and two sites in Long and Narrow lakes, respectively, RATIO was greater than 1.8; at these sites, P release from sediments to lakewater could be hindered.

[SRP] in lakewater above the sediment-water interface (LWP) were generally greater than [SRP] in the trophogenic zone (Table 4.1 and 4.2). This indicates that lakewater just above the shallow sediments (a) is not fully mixed with trophogenic lakewater, and (b) may be influenced by P release from sediments. Thus, shallow sediment characteristics were compared to both LWP and TZP.

Simple correlations between sediment parameters and [TP]

Porewater or particulate sediment parameters were not correlated with TZP in the seven study lakes (Table 4.4). However, TZP was positively correlated with LWP and $[Fe^{2+}]$ in lakewater just above shallow sediments (Table 4.4, Fig. 4.2a). LWP was positively correlated to average [SRP] and pH in porewater, and to FLUX (Table 4.4). However, LWP was negatively correlated with RATIO (Table 4.4; Fig. 4.2b). Although RATIO is generally less than 1.8, the negative relationship between LWP and RATIO indicates that release of P from porewater to

lakewater may be regulated by the abundance of Fe relative to P. The relationships with LWP suggest that porewater [SRP], FLUX and RATIO may indirectly explain some of the lake-to-lake variation in trophic status.

Principal Component Analyses

The PCA included particulate P fractions, POR, pH, RATIO and FLUX. The first two principal components (PC) explained 78.1% of the total variance of these data. The remaining six principal components explained 21.9% of the variance. These six PC's had eigenvalues less than 1, and were therefore not considered important (Harris, 1979). The first PC (PC1) explained 51.6% of the orginal variance and represented mainly particulate sediment parameters. The second PC (PC2) explained 26.5% of the original variance and represented mainly FLUX, RATIO and porewater pH (Table 4.5). The important variables in PC2 indicate the mobility of porewater P: FLUX as potential P release to lakewater by molecular diffusion, RATIO as an indication of P sorption onto Fe (negative weight on PC2), and pH as an indication of decreased adsorption onto sediments (Ku et al., 1978). PC1 and PC2 distinguished the lakes and some sites per lake from each other (Fig 4.3). Average factor scores of PC1 were not correlated with either LWP or to TZP ($P > 0.5$ and 0.1, respectively). Average factor scores (per site) of PC2 were significantly correlated with LWP ($df = 20$, $r = 0.75$, $P < 0.001$). This relationship explained slightly more variance than the simple relationship between RATIO and LWP: i.e., r improved from 0.71 to 0.75. In addition, average factor scores per lake for PC2 were significantly correlated with TZP ($df = 5$, $r = 0.77$, $P < 0.05$). This suggests that porewater parameters were related to TZP; no such relationship was found with simple correlations (Table 4.4).

Relationships of both TZP and LWP with mobile P (PC2) suggest that P exchange between porewater and lakewater may influence the TP concentration in the trophogenic zone.

4.5 CONCLUSION

Concentrations of SRP in lakewater above the sediments (LWP) were correlated with [SRP], pH and molar ratio of Fe:P (RATIO) in porewater. However, these porewater variables explained, at most, half the variance of LWP. In a principal component analysis, slightly more variance of LWP was explained by mean factor scores of PC2 (a mobile porewater P component) than by a simple correlation. This suggest that other variables, in addition to those measured in this study (i.e., Fe, Ca in particulate sediments, biological activity, mixing), are important in regulating the exchange of P between sediments and lakewater. No simple correlations were found between sediment parameters and total P concentrations in the trophogenic zone (TZP). An indirect link between sediments and trophogenic lakewater (i.e., between porewater [SRP] and LWP, and between LWP and TZP) suggests that the relationship between the two compartments is complex. However, mean factor scores per lake of PC2 (a mobile porewater P component) were correlated with TZP. Thus, sediment characteristics may be related to TZP.

Previous studies have failed to find a relationship between sediment and lakewater characteristics (Hakanson, 1984; Ostrofsky, 1987). Exchange of P between sediments and lakewater by sediment P release should be especially important in lakes with small external P inputs. In the study area, effective drainage basins are small, and

there is relatively little P input from surface runoff. In addition, I sampled shallow sediments; P release from these sediments directly affects P concentrations in the trophogenic zone. Both these factors probably contributed to the relationship found between sediment and trophogenic lakewater characteristics in the study lakes. This study indicates that (1) shallow sediments may be important in regulating trophic status of lakes in central Alberta, and (2) shallow sediments should not be ignored as a potential P source to lakes.

4.6 REFERENCES

Alberta Environment (1986) Minnie Lake Stabilization Study. Summary Report, Planning Division, Edmonton, Canada.

APHA (1980) Standard Methods for Examination of Water and Wastewater, 15th edition. American Public Health Association, Washington, D.C.

Bostrom B., Jansson M. and Forsberg C. (1982) Phosphorus release from lake sediments. Arch. Hydrobiol. 18, 5-59.

Carignan R. (1984) Interstitial water sampling by dialysis: methodological note. Limnol. Oceanogr. 29, 667-670.

Carlton R. G. and Wetzel R. G. (1988) Phosphorus flux from lake sediments: effect of epipelic algal oxygen production. Limnol. Oceanogr. 33, 562-570.

Dixon W. J. (1983) BMDP Statistical Software. Univ. of California Press, Berkely.

Fee E. J. (1979) A relation between lake morphometry and primary productivity and its use in interpreting whole-lake eutrophication experiments. Limnol. Oceanogr. 24, 401-416.

Green R. (1972) Geological Map of Alberta. Research Council of Alberta map (scale 1:1,267,000), Edmonton, Canada.

Green R. H. and Vascotto G. L. (1978) A method for the analysis of environmental factors controlling patterns of species composition in aquatic communities. Wat. Res. 12, 583-590.

Hakanson L. (1984) On the relationship between lake trophic status and lake sediments. Wat. Res. 18, 303-314.

Harris R. J. (1975) A Primer of Multivariate Statistics. Academic Press Inc., New York.

Hesslein R. H. (1976) An in situ sampler for close interval pore water studies. Limnol. Oceanogr. 21, 912-914.

Hutchinson G. E. (1957) A Treatise on Limnology. Wiley, New York.

Kjearsgaard A. A. (1972) Soil Survey of Tawatinaw (83-I). University of Alberta Bull. No. SS-12, Edmonton, Canada.

Ku W. C., DiGiano F. A. and Feng T. H. (1978) Factors affecting phosphate adsorption equilibria in lake sediments. Wat. Res. 12, 1069-1074.

Lijklema L. (1977) The role of iron in the exchange of phosphate between water and sediments. In Proceedings of the 1st Symposium on the Interactions between Sediments and Freshwater (Edited by Golterman H. L.), pp. 313-317. Junk, The Hague.

Logan T. J., Oloya T. O. and Yaksich S. M. (1979) Phosphate characteristics and bioavailability of suspended sediments from streams draining into Lake Erie. J. Great Lakes Res. 5, 112-123.

Mawhinney M. R. and Bisutti C. (1987) Common Corers and Grab Samplers Operating Manual. (Available through Technical Operations). National Water Research Institute, Burlington, Canada.

Mayer T. and Williams J. D. H. (1981) Modified Procedure for Determining the Forms of Phosphorus in Freshwater Sediments. Environment Canada, Technical Bull. No. 119, Burlington, Canada.

Mortimer C. H. (1941) The exchange of dissolved substances between mud and water in lakes. J. Ecol. 29, 280-329.

Murphy J. and Riley J. P. (1962) A modified single solution method for the determination of phosphate in natural waters. Analytica chim. Acta 27, 31-36.

Ohle W. (1964) Interstitiallosungen der Sedimente, Nahrstoffgehalt des

Wassers und Primarproduktion. Helgol. Wiss. Meeresunters. 10, 411-429.

Ostrofsky M. (1987) Phosphorus species in the surficial sediments of lakes of eastern North America. Can. J. Fish. Aquat. Sci. 44, 960-966.

Prepas E. E. (1983) Orthophosphate turnover time in shallow productive lakes. Can. J. Fish. Aquat. Sci. 40, 1412-1418.

Prepas E. E., Dunnigan M. E. and Trimbee A. M. (1988) Comparison of in situ estimates of chlorophyll a obtained with Whatman GF/F and GF/C glass-fiber filters in mesotrophic to hypereutrophic lakes. Can. J. Fish. Aquat. Sci. 44, 910-914.

Sokal R. R. and Rohlf F. J. (1981) Biometry. 2nd edition. Freeman, San Francisco.

Sommers L. E., Harris R. F., Williams J. D. H., Armstrong D. E. and Syers J. K. (1972) Fractionation of organic phosphorus in lake sediments. Soil Sci. Soc. Amer. Proc. 36, 51-54.

Stauffer R. E. and Armstrong D. E. (1984) Lake mixing and its relationship to epilimnetic phosphorus in Shagawa Lake, Minnesota. Can. J. Fish. Aquat. Sci. 41, 57-69.

Strong W. L. and Leggat K. R. (1981) Ecoregions of Alberta. Alberta Energy and Natural Resources, ENR Technical Rep. No. T/41, Edmonton, Canada.

Tessenow U. (1972) Losungs-, Diffusions- und Sorptions-Prozesse in der Oberschicht von Seesedimenten. Part 1. Arch. Hydrobiol. Suppl. 38, 353-398.

Tessenow U. (1974) Losungs-, Diffusions- und Sorptions-Prozesse in der Oberschicht von Seesedimenten. Part 4. Reaktionsmechanismen und

Gleichgewichte im System Eisen-Mangan-Phosphat im Hinblick auf die Vivianitakkumulation im Ursee. Arch. Hydrobiol. Suppl. 38, 353-398.

Trew D. O., Beliveau D. J. and Yonge E. I. (1987) The Baptiste Lake Study. Technical Report, Water Quality Control Branch, Pollution Control Division, Alberta Environment, Edmonton, Canada.

Trew D. O., Yonge E. I. and Kaminski R. P. (1981) A Preliminary Trophic Assessment of Nine Lakes in the Cold Lake Region. Water Quality Control Branch, Pollution Control Division, Alberta Environment, Edmonton, Canada.

Wetzel R. G. (1983) Limnology. 2nd ed. Saunders, Philadelphia.

Williams J. D. H., Shear H. and Thomas R. L. (1980) Availability to Scenedesmus quadricauda of different forms of phosphorus in sedimentary materials from the Great Lakes. Limnol. Oceanogr. 25, 1-11.

Table 4.1. Location, surface area (A_0), maximum depth (z_{max}), depth of the thermocline or bottom of the trophogenic zone (TZ) during the summer (whichever was deeper; z_{mix}), conductivity (Cond) and mean summer total and soluble reactive phosphorus (TZP and SRP, respectively) concentrations in TZ of seven study lakes. Blanks indicate no data available.

Lake	°N	°W	A_0	z_{max}	z_{mix}	Cond	TZP	SRP
			km^2	m		$uS.cm^{-1}$	$mg.m^{-3}$	
Baptiste[1,2]	54°45'	113°33'	4.6	26	5	320	38	2
Island[1,2,3]	54°52'	113°31'	1.0	15	8.5	370	20	3
Jenkins[3]	54°55'	113°36'	1.8	18	8	244	25	
Long[3]	54°34'	113°38'	1.6	28	10	312	13	
Minnie[2,4]	54°17'	111°07'	0.8	24	9	992	34	4
Narrow[3,5]	54°35'	113°37'	1.1	36	12	290	11	0.8
Tucker[6]	54°32'	110°37'	7.2	7	7	387	42	12

References: 1 Trew et al. (1987); 2 D. O. Trew, Alberta Environment, unpubl. data; 3 Prepas et al. (1988); 4 Alberta Environment (1986); 5 Prepas (1983); 6 Trew et al. (1981).

Table 4.2. Mean and one standard error (in brackets) of SRP and Fe^{2+} concentrations in lakewater and porewater, and porewater pH within 10 cm of the sediment-water interface at the seven study lakes. The average molar ratio of Fe^{2+}:SRP (RATIO) in porewater, potential release of P from sediments to lakewater by molecular diffusion (FLUX in mg $P.m^{-2}.d^{-1}$) and the depths of the sites sampled are indicated.

	Lakewater			Porewater				
Lake,	SRP	Fe^{2+}	pH	SRP	Fe^{2+}	RATIO	pH	FLUX
Depth	$mg.m^{-3}$			$mg.m^{-3}$				
Baptiste 2.5,5m	19(6)	58(11)	8.1	456(65)	255(36)	0.4(0.1)	7.9	0.3
Island 2.5,4,5,7.5m	9(4)	44(10)	8.0	282(56)	232(8)	0.8(0.1)	8.0	0.1
Jenkins 4,5,7.5m	43(13)	68(19)	8.2	1960(157)	360(36)	0.1(0.0)	8.0	0.5
Long 2.5,4,5m	4(2)	51(16)	8.2	249(37)	942(229)	2.4(0.6)	7.9	0.4
Minnie 5,7.5m	29(22)	93(7)	9.3	1009(201)	977(146)	0.7(0.1)	9.5	1.5
Narrow 2.5,5,7.5,10m	6(0)	38(9)	8.0	68(10)	250(57)	2.1(0.3)	7.8	0.04
Tucker 2.5,4,5,7m	44(15)	120(57)	9.2	356(75)	166(16)	0.3(0.1)	9.0	0.2

Table 4.3. Mean and one standard error (in brackets) of water content (POR) and phosphorus fractions in the top 10 cm of bottom sediments collected from the seven study lakes: depths as in Table 4.2.

Lake	POR	CDB-P	NaOH-P	HCl-P	ORG-P
Baptiste	52 (6)	86 (6)	14 (2)	152 (10)	131 (49)
Island	42 (7)	132 (48)	15 (4)	174 (26)	92 (29)
Jenkins	28 (4)	121 (16)	8 (1)	191 (29)	18 (5)
Long	87 (2)	300 (46)	30 (2)	210 (11)	231 (21)
Minnie	85 (2)	232 (22)	24 (2)	405 (14)	125 (23)
Narrow	44 (3)	73 (7)	8 (1)	139 (8)	41 (3)
Tucker	64 (8)	351 (64)	21 (4)	194 (27)	139 (27)

Table 4.4. Correlation coefficients between (a) transformed particulate sediment parameters, SRP, Fe^{2+} and pH in porewater and lakewater above the sediment-water interface, RATIO and FLUX, and TP concentrations in the trophogenic zone (TZP), and (b) particulate and porewater parameters, and SRP in lakewater above the sediment-water interface (LWP).

		TZP (df = 5)	LWP (df = 20)
Lakewater SRP		0.856 *	
	Fe^{2+}	0.811 *	
	pH	0.629	
Porewater SRP		0.626	0.502 *
	Fe^{2+}	-0.211	-0.186
	pH	0.618	0.442 *
	RATIO	-0.746	0.712 ***
FLUX		0.543	0.433
POR		0.033	0.044
NaOH-P		0.223	0.149
CDB-P		0.274	0.362
HCl-P		0.343	0.330
ORG-P		0.179	0.014

*,*** significant at $P < 0.05$ and 0.001, respectively.

Table 4.5. Rotated factor loadings of particulate and porewater variables on the two important principal components (PC1 and PC2) in a principal component analysis.

Variable	PC1	PC2
POR	0.952	0.217
ORG-P	0.906	-0.040
NaOH-P	0.896	0.229
CDB-P	0.831	0.388
HCl-P	0.646	0.509
FLUX	0.364	0.803
RATIO	0.556	-0.715
Porewater pH	0.219	0.673
	-----	-----
Variance explained	4.127	2.120
% of total variance	51.6	26.5

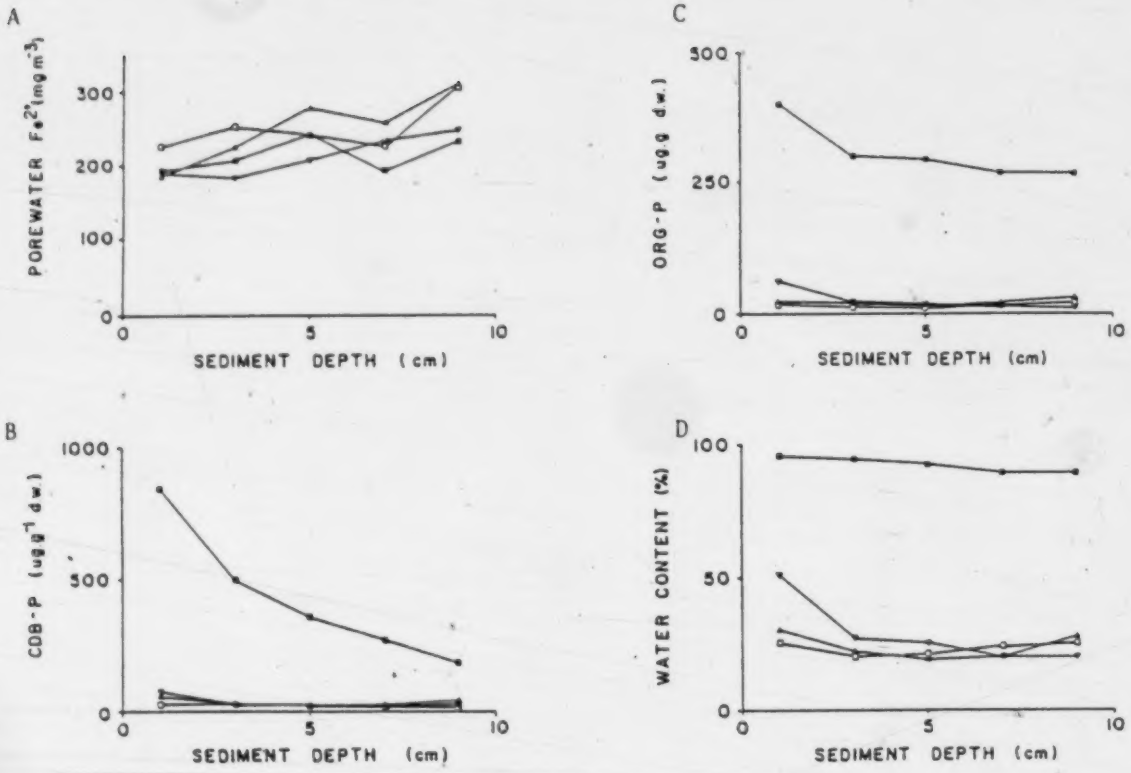


Figure 4.1. Porewater ferrous iron (Fe^{2+}; a), and sediment CDB-P (b), ORG-P (c) and water content (d) in the top 10 cm of sediment from Island Lake. Data from four sites are presented:
□ 2.5-m, ▲ 4-m, ▽ 5-m, and ■ 7.5-m depth.

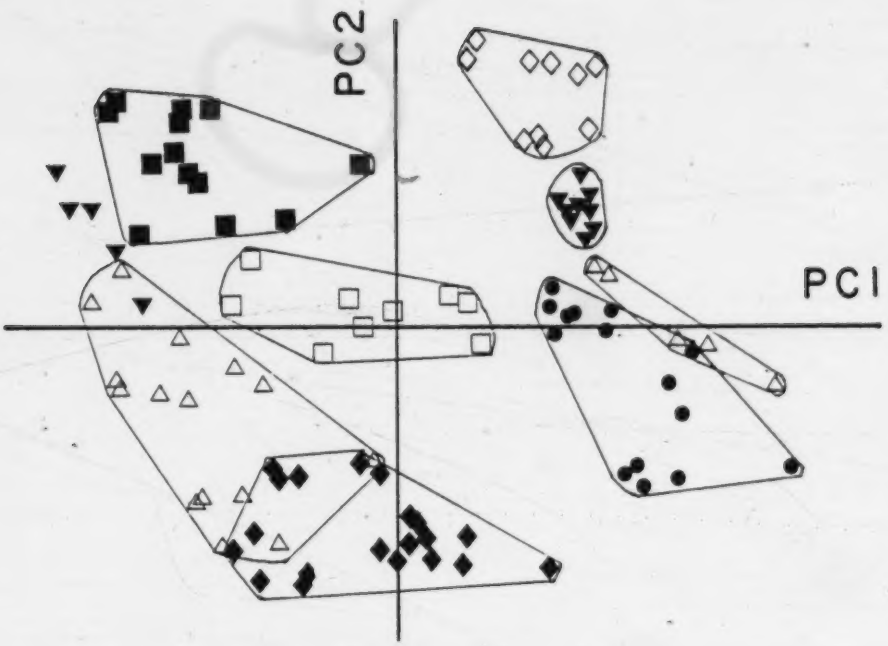
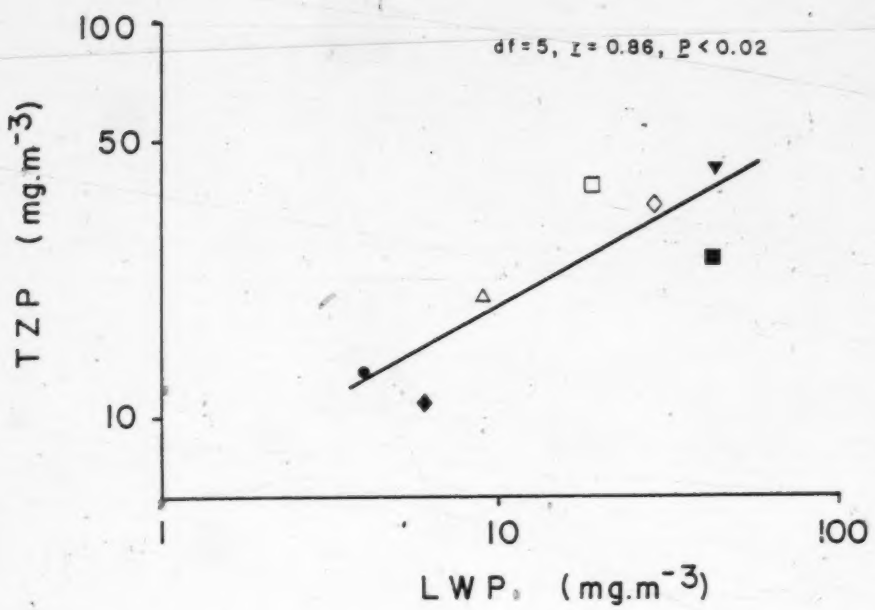


Figure 4.2. Simple correlations between (a) total P concentrations in the trophogenic zone (TZP) and [SRP] in lakewater above the sediments (LWP), and (b) LWP and molar ratio of Fe^{2+} to SRP in porewater (RATIO). Lakes are indicated with the following symbols: Baptiste □, Island △, Jenkins ■, Long ●, Minnie ◇, Narrow ◆, and Tucker ▼. Solid lines indicate the regression lines.



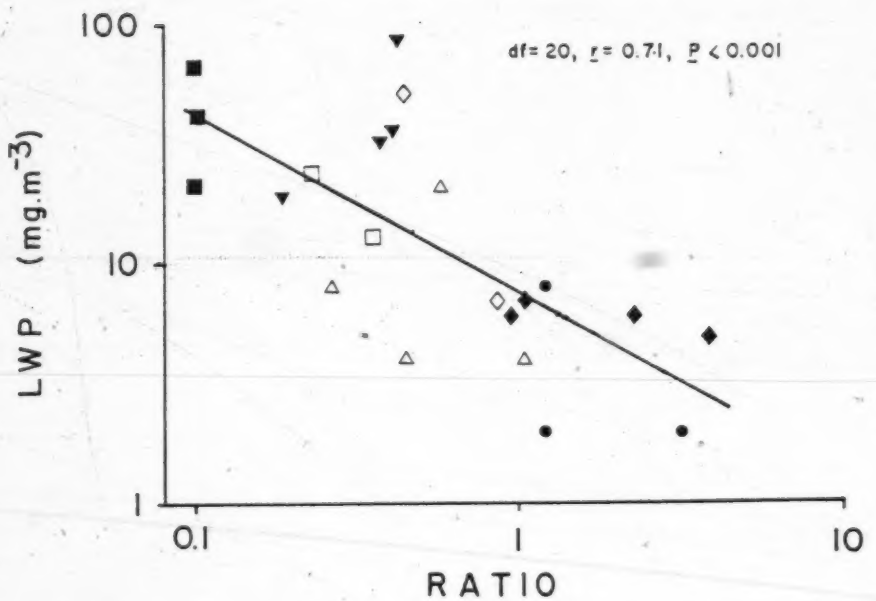


Figure 4.3. Separation of study lakes by the two important principal components (PC1 and PC2) based on sediment and porewater characteristics. Abbreviations and symbols are as in Fig. 4.2.

5. POTENTIAL SIGNIFICANCE OF PHOSPHORUS RELEASE FROM SHALLOW SEDIMENTS OF DEEP ALBERTA LAKES[1]

5.1 ABSTRACT

The potential importance of internal phosphorus (P) sources from shallow sediments (i.e., within the trophogenic zone) to the trophogenic zone was investigated in 16 Alberta lakes. Comparison of total P (TP) mass determined directly from field measurements (TP_o) during summer and the mass estimated from short-term TP budgets (TP_e) disclosed that TP_o was, on average, significantly greater than TP_e ($\underline{P} < 0.0005$). For eight lakes where vertical gradients of TP could be calculated across the bottom of the trophogenic zone, average TP transport from the hypolimnion to the trophogenic zone represented less than 2% of the missing TP ($TP_d = TP_o - TP_e$). In situ soluble reactive P (SRP) concentrations in sediment porewater and overlying lakewater indicated that P release by molecular diffusion from shallow sediments represented, on average, 13% of TP_d. While this source is still low, transport by groundwater, turbulent mixing and bioturbation within shallow sediments could potentially account for the unexplained TP_d. The importance of shallow sediments as a P source to the trophogenic zone is further supported by the observation that, in 14 lakes, TP_d was strongly correlated with a combination of lake trophic status and extent of shallow sediments ($\underline{P} < 0.001$). This is the first study to estimate the potential contribution of P release from shallow sediments to the

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trophogenic zone in several deep lakes. Average TP_d in the study lakes was 2.2 $mg.m^{-2}.d^{-1}$, which is much greater than TP input by atmospheric deposition (0.18 $mg.m^{-2}.d^{-1}$) and similar to runoff from the watershed (2.1 $mg.m^{-2}.d^{-1}$). Shallow sediments represent a potentially significant P source to the trophogenic zone, especially for naturally eutrophic lakes; P release from these sediments has direct implications for lake management.

5.2 INTRODUCTION

Although bottom sediments may represent a major source of the limiting nutrient phosphorus (P) to lakewater, this potential contribution is difficult to assess (e.g., Stauffer 1987). This difficulty is due, in part, to the fact that P release from bottom sediments can occur into aerobic and anaerobic lakewater and that both these release rates are temperature dependent (Kamp-Nielsen 1975). In shallow lakes (i.e., lakes without a strong thermal gradient during summer), lakewater just above the sediments can alternate between an anaerobic and aerobic state over short time periods, and, at any time, both states can co-occur (Bengtsson 1975; Bostrom et al. 1985). In shallow lakes, P released from sediments can be mixed throughout the water column during most of the ice-free period; the separate contribution of sediment P release into anaerobic and aerobic lakewater can not be accurately assessed.

In deep lakes (i.e., lakes with a strong thermal gradient during summer), the surface of the sediments below the trophogenic zone is relatively cool and can be aerobic or anaerobic. However, P released

from these sediments generally does not enter the trophogenic zone during summer (Schindler et al. 1977, 1980; Stauffer and Armstrong 1984). The surface of shallow sediments (i.e., within the trophogenic zone) in deep lakes is generally warm and aerobic during summer; the potential for P release from these sediments on the trophogenic zone can be investigated with detailed, short-term P budgets (i.e., during summer). Nevertheless, few short-term P budgets have been calculated for the trophogenic zone of deep lakes, with a focus on sediment P release. Instead, the residual term in these budgets has been used to estimate P sedimentation, P transport from the hypolimnion, or external P loading from the watershed (Schindler et al. 1973; Vollenweider 1976; Kortmann et al. 1982). Only two short-term P budgets calculated for deep lakes included direct measurements of external inputs, outputs and sedimentation and independent estimates of P transport from the hypolimnion (Lie 1977; Caraco et al. 1988). In both cases, substantially more P was measured in or lost from the epilimnion than was predicted from P budgets. P release from shallow sediments into the trophogenic zone is one likely source of this missing P; this release may be a significant source of P to the trophogenic zone of many deep lakes (Rigler 1974; Fee 1979; Stauffer 1987).

To investigate the potential release of P from shallow sediments, I compared the observed P mass with that predicted from short-term P budgets for the trophogenic zone of 16 deep lakes in central Alberta. Up to seven years of P data were available for each lake; in total, 36 P budgets were calculated. Differences between the observed and predicted P mass were then compared to potential P transport from the hypolimnion and from shallow sediments to the trophogenic zone of select lakes.

These calculations allowed me to compare the potential contribution of hypolimnetic and shallow sediments to P in the trophogenic zone of deep Alberta lakes.

5.3 MATERIALS AND METHODS

Study lakes

The 16 study lakes are in the mixed-wood section of the boreal forest in central Alberta. All lakes are situated on sedimentary bedrock overlain with drift (Green 1972; Kjearsgaard 1972). The climate in the study area is continental. Average annual precipitation and lake evaporation are 503 mm and 636 mm, respectively; annual runoff in the area is relatively low, 50 to 100 mm (Hydrology Branch, Alberta Environment, Edmonton, Alta, unpubl. data). Surface area of the lakes varied from 0.1 to 36 km^2; mean depth varied from 4 to 16 m. Lake trophic status ranged from meso-eutrophic to eutrophic: mean summer trophogenic total P (TP) varied from 11 to 38 $mg.m^{-3}$ (Wetzel 1983; Table 5.1). Drainage basin areas varied from 0.6 to 537 km^2. Several upstream lakes were present in some drainage basins. The drainage basins of Amisk and Marie lakes each contained two upstream lakes; Twin Lake contained one upstream lake (short-term P budgets were not calculated for these upstream lakes). Four study lakes drained into three other lakes: Hilda and Marie drained into Ethel Lake, Moore into Hilda Lake, and Narrow into Long Lake. Six lakes were headwater lakes.

During summer, water in all 16 lakes was thermally stratified. The trophogenic zone was defined as the stratum where light penetration was greater than 1% of surface irradiance, or less than twice the Secchi

disc depth, and the epilimnion as the stratum above the thermocline. At 13 lakes, the trophogenic zone and the epilimnion extended to the same depth. In one lake (Baptiste), the epilimnion extended 1 to 3 m below the trophogenic zone. Because water in the trophogenic zone mixed regularly with epilimnetic water at Baptiste Lake, I equated the trophogenic zone with the epilimnion in this lake; the volume of water and total P (TP) in the epilimnion were used in subsequent calculations for the trophogenic zone. Water below the trophogenic zone in all lakes was referred to as the hypolimnion. At two lakes (Long and Narrow), the trophogenic zone extended below the thermocline; thus, the trophogenic zone was not separated from the hypolimnion by the thermocline. Since TP transport from the hypolimnion to the trophogenic zone is inhibited by a strong thermal gradient, this route would be easier at Long and Narrow lakes than at the other study lakes. Shallow sediments were defined as sediments within the trophogenic zone.

Summer was defined as the period between spring and fall turnover to ensure that deep mixing events or spring runoff did not affect TP concentrations ([TP]) in the trophogenic zone. During summer (May 23 to August 26, 1980 to 1987), the extent of the trophogenic zone was determined. Water samples were collected from this zone and analyzed for TP, 3 to 13 times per summer at each lake (Prepas 1983; E. E. Prepas, unpubl. data; D. O. Trew, Alberta Environment, Edmonton, Alta, unpubl. data). At 11 lakes, TP concentrations ([TP]) were measured during one summer only; at five lakes (Amisk, Baptiste, Ethel, Long, and Narrow), appropriate data were collected over two to seven summers. Baptiste and Island lakes have two distinct basins (one shallow and one deep basin); budgets were calculated only for the deep, thermally

stratified basins of these lakes. Amisk Lake has two deep basins; [TP] from each basin were weighted according to their respective volumes and pooled to calculate a whole-lake [TP]. The other 13 lakes had only one basin.

Short-term P budgets

The following morphometric parameters were required to calculate short-term P budgets for each lake: size of drainage basin (A_d), lake surface area (A_0), and volume of water in the trophogenic zone (V_{mix}). These data were obtained from several sources (Babin 1984; D. O. Trew, Alberta Environment, Edmonton, Alta, unpubl. data; E. E. Prepas unpubl. data; Hydrology Branch, Alberta Environment, Edmonton, Alta, unpubl. data) or were determined with a digital planimeter from (1:50,000) topographic maps and bathymetric maps (Table 5.1).

Daily TP budgets (in mg) were calculated for each of the 16 lakes:

$$TP_{m(x+1)} = TP_{m(x)} + TP_{a(x)} + TP_{r(x)} - TP_{s(x)} - TP_{o(x)} \qquad (1)$$

$TP_{m(x+1)}$ and $TP_{m(x)}$ are the TP mass in the trophogenic zone for day(x+1) and the previous day(x). TP_a and TP_r are daily loads of TP to the trophogenic zone from atmospheric deposition directly onto the lake surface and runoff from the drainage basin, respectively. TP_s and TP_o are daily losses of TP from the trophogenic zone by sedimentation and surface outflow, respectively.

Additions of TP to the trophogenic zone from external sources were determined as follows: TP_a was estimated from monthly atmospheric deposition rates (wet and dry fallout), measured in central Alberta from 1983 to 1986 (Shaw et al. 1989; Table 5.2), and multiplied by lake

surface area (A_o, Table 5.1). These deposition rates are similar to those measured in other central Alberta lakes (Mitchell 1985; Trew et al. 1987). For 1983 to 1986, deposition rates were used from the same year [TP] was determined in the study lakes. Average monthly deposition rates from 1983 to 1986 were used for lakes sampled in 1980, 1981, 1982 and 1987. For 15 lakes, TP_r was estimated following the procedure in Dillon and Rigler (1975); 0.079 and 0.150 $mg.m^{-2}.d^{-1}$ were the export coefficients used for forested and other areas, respectively. The export coefficient for forested areas was the average measured in two forested watersheds in central Alberta from May to August (Munn and Prepas 1986), and is similar to other coefficients for forested areas on sedimentary bedrock (Dillon and Kirchner 1975; Mitchell 1985). The export coefficient for non-forested areas (cultivated or cleared) is 1.9 times that for forested areas and is based on the average ratio of P export from non-forested to forested areas that drained into a lake in central Alberta (Mitchell 1985). For Baptiste Lake, measured data collected from 1976 to 1978, were used to estimate average TP_r (Trew et al. 1987).

Upstream lakes trap nutrients from their drainage basin, and reduce export to downstream lakes (Dillon and Rigler 1975). TP retention in upstream lakes was calculated from an empirical equation determined for lakes with low areal water loading (Ostrofsky 1978):

$$R = 0.201\ e^{-0.0425*q} + 0.574\ e^{-0.00949*q} \qquad (2),$$

in which R is the retention coefficient, and q is the areal water load (annual lake outflow in m^3 divided by A_o in m^2). The annual outflow

volume was determined from hydrological budgets as the difference between water loss by evaporation from the lake and the sum of runoff from the drainage basin and precipitation on the lake (Hydrology Branch, Alberta Environment, Edmonton, Alta, unpubl. data). External P inputs to upstream lakes were calculated as described for the study lakes. TP export from upstream lakes into downstream study lakes was calculated as (1-R) times the external TP load to the upstream lake.

Losses of TP from the trophogenic zone were determined as follows: Sedimentation of TP was estimated as 2 % of TP_m per day; this was the measured rate determined at one of the study lakes during the summer of 1985 (E. E. Prepas, unpubl. data). Outflow of TP was calculated as [TP] in the trophogenic zone (i.e., TP_m divided by V_{mix}) was multiplied by daily outflow volume. Outflow in the study area depends on lake elevation, which lags days or weeks behind or follows precipitation patterns (Trew et al. 1987; Shaw et al. 1989). Since hydrological budgets were based on long-term data, monthly outflow volumes were assumed to follow long-term monthly precipitation averages. Monthly precipitation in May, June, July, and August was 7.9, 14.3, 17.0, and 15.1% of annual precipitation, respectively (Hydrology Branch, Alberta Environment, Edmonton, Alta, unpubl. data). Daily outflow rates were calculated from monthly volumes. At Peanut Lake, annual outflow from the hydrological budget was negative; a daily outflow of 0 was used in my calculations.

Daily budgets for TP in the trophogenic zone were calculated for consecutive days between sampling dates: $TP_{m(x)}$ for one day was substituted with $TP_{m(x+1)}$ from the previous day (Eq. 1). To calculate TP_m at each sampling date, observed [TP] was multiplied by V_{mix}. At

each sampling date, TP_m measured on that date ($TP_{m,o}$ in mg) was compared to TP_m estimated ($TP_{m,e}$ in mg) with daily budgets since the previous sampling date. The difference between observed and expected TP_m was expressed as an areal rate (TP_{dif} in $mg.m^{-2}.d^{-1}$):

$$TP_{dif} = \frac{TP_{m,o} - TP_{m,e}}{t\ A_0} \qquad (3),$$

in which t is the number of days between sampling dates. Since [TP] was measured at variable intervals, t varied. TP_{dif} was weighted according to the respective sampling interval (t) and pooled. An average TP_{dif} (TP_d) was calculated for each year data were available for a lake.

P release from the hypolimnion

Vertical profiles of TP in eight study lakes (Prepas unpubl. data) were analyzed to determine the average TP gradients during the summer between the hypolimnion and the trophogenic zone. Eddy diffusion of TP (F in $mg.\ m^{-2}.d^{-1}$) was calculated:

$$F = D\ .\ dC/dx\ .\ 86400 \qquad (4),$$

where D is the eddy diffusion coefficient (in $m^2.s^{-1}$), dC/dx the average [TP] gradient during summer (in $mg.m^{-4}$), and 86400 the factor converting s to d. When TP gradients from hypolimnion to trophogenic zone were negative, F was assumed to be 0. For six lakes, the thermocline coincided with the bottom of the trophogenic zone; eddy diffusion of TP across the thermocline was calculated with $D = 8x10^{-8}\ m^2.s^{-1}$ (Quay et al. 1980). At Long and Narrow lakes, where the trophogenic zone

extended below the epilimnion, eddy diffusion of TP was calculated with $D = 1.8 \times 10^{-6}$ $m^2.s^{-1}$ (Quay et al. 1980).

P release from shallow sediments

During the summer of 1986, porewater samples were collected once from Island, Long, and Minnie and twice from Baptiste and Narrow lakes. Sediment porewater was collected *in situ* with Plexiglass peepers, fitted with Gelman HT-450 membrane filters. These peepers were slightly modified from Hesslein (1976): each side consisted of 25 chambers. Peepers were prepared as outlined in Carignan (1984) with minor modifications (Chapter 2). Exposure of peepers and porewater samples to air was kept to a minimum or prevented in a N_2 environment.

At these five lakes, porewater was collected from two to four depths within the trophogenic zone. Water samples from both sides of the peeper were stored on ice and analyzed separately. To determine the P gradient across the sediment-water interface, two samples were collected: lakewater pooled from five to ten chambers immediately above the sediment-water interface, and porewater from 0 to 2 cm below the sediment-water interface. Aliquots from these samples were diluted 5 to 25 times with double distilled water, and analyzed for soluble reactive P (SRP) within 12 h after collection (Murphy and Riley 1962). The average [SRP] from the two sides of a peeper was used in subsequent analyses. Gradients of SRP across the sediment-water interface were calculated from [SRP] in lakewater and porewater (Chapter 2).

To determine sediment water content, three sediment cores were collected at most peeper sites. They were sectioned in the field in 2-cm intervals and water content was determined for the top 2 cm of the sediment by drying at 60°C for 2 d. Average water content (by weight)

of the three sections from each site was used to calculate water content by volume: 1.191 or 1 times water content by weight for sediments less than or greater than 90 % water content by weight, respectively (determined from sediments of the study lakes).

The diffusive flux of P from shallow sediments was calculated according to Berner (1980):

$$J = \phi \cdot D \cdot \theta^{-2} \cdot dC/dx \cdot 86400 \qquad (5).$$

J is the SRP flux across the sediment-water interface (in $mg.m^{-2}.d^{-1}$). ϕ is the water content by volume. D is the diffusion coefficient (1.24×10^{-9} $m^2.s^{-1}$; Quigley and Robbins 1986). θ^2 is a tortuosity term calculated as ϕ^{1-n}, with n = 1.8 (Berner 1980). dC/dx is the SRP gradient across the sediment-water interface (in $mg.m^{-4}$; dx = 0.015 m). 86400 is the factor converting s to d. Statistical tests are from Sokal and Rohlf (1981).

5.4 RESULTS

Short-term P budgets

In total, 36 TP budgets were calculated for the trophogenic zone of 16 lakes. For 35 of the 36 budgets, the mass of TP measured on sampling dates was different from that calculated with short-term TP budgets. Expressed over lake surface area, these differences (TP_d) ranged from -4.1 to 16.8 $mg.m^{-2}.d^{-1}$ (average = 2.2 $mg.m^{-2}.d^{-1}$; Table 5.3). In 32 of 36 budgets, TP_d was positive. In three of the 36 budgets, TP_d was negative: the budget for Twin Lake and two of the four budgets for Amisk

Lake. When all data were included, discrepancies in the budgets (TP_d) were significantly greater than 0 $mg.m^{-2}.d^{-1}$ ($\underline{t}$-test: df = 35, $\underline{t}$ = 4.3, $\underline{P} < 0.0005$); more TP was measured in the trophogenic zone than was estimated with short-term budgets (Eq. 3).

Phosphorus release from the hypolimnion

For eight lakes where vertical profiles of TP in the water column were available, average TP gradients from the hypolimnion to the trophogenic zone varied from -14.3 to 18.4 $mg.m^{-4}$, at Sauer and Island lakes, respectively (Table 5.4). Average release rates of TP from the hypolimnion into the trophogenic zone (expressed over A_0) varied from 0 $mg.m^{-2}.d^{-1}$ at Sauer Lake to 0.05 $mg.m^{-2}.d^{-1}$ at Amisk and Island lakes (Table 5.4). On average, TP transport from the hypolimnion into the trophogenic water for all eight lakes was less than 2% of TP_d (Table 5.4).

P release from shallow sediments

Concentrations of SRP just above the shallow bottom sediments ranged from 2 to 50 $mg.m^{-3}$ at Long and Minnie lakes, respectively (Table 5.5). At all sites, porewater [SRP] in the top 2 cm of the sediment was greater than [SRP] just above the sediment-water interface: porewater [SRP] varied from 11 to 1232 $mg.m^{-3}$ at Long and Minnie lakes, respectively. SRP gradients across the sediment-water interface varied from 470 to 77800 $mg.m^{-4}$ at Narrow and Minnie lakes, respectively (Table 5.5); the area-weighted SRP gradient across the sediment-water interface varied from 1830 to 30810 $mg.m^{-4}$ (Table 5.6).

Water content in bottom sediments varied from 25 to 96% (by weight), the extremes were both from Island Lake (Table 5.5). Area-

weighted water content (by volume) varied from 43 to 94% at Baptiste and Minnie lakes, respectively (Table 5.6). Expressed over the entire lake, average release rates of P by molecular diffusion (Eq. 5) ranged from 0.03 to 1.5 $mg.m^{-2}.d^{-1}$. Release rates of P by molecular diffusion were, on average, 13% of TP_d calculated from short-term P budgets (during 1986) for these five lakes (Table 5.6).

5.4 DISCUSSION

Short-term P budgets

In 32 of 36 short-term P budgets for 16 lakes, less TP was projected in the trophogenic zone than was observed. These differences could be due to: (a) underestimates of atmospheric deposition and/or runoff of TP, (b) overestimates of sedimentation and/or outflow of TP, or (c) exclusion of internal TP sources (i.e., from the hypolimnion or shallow sediments).

Atmospheric deposition of TP was measured directly in the study area (Shaw et al. 1989). Although daily atmospheric deposition rates will vary from monthly averages (as could other monthly averages used in Eq. 1), these discrepancies will balance each other out and should not influence TP_d in any consistent direction.

Runoff of TP from the watershed (TP_r) was overestimated with export coefficients in 15 of 16 lakes. Ponding of water occurs in marshy areas, behind beaver dams and other areas of low relief, which are all common in the study area. These areas do not contribute to TP_r since they do not drain into a study lake in years of average runoff (Meid and Miller 1978). For example, the measured TP input from surface runoff

during 1976 to 1978 at Baptiste Lake was only 37 % of TP_r, calculated with the same export coefficients used for the other study lakes (Trew et al. 1987). Consequently, TP_d was relatively higher at Baptiste Lake compared to the other study lakes. Annual estimates of TP_r from upstream lakes into Ethel Lake, based on my export coefficients, were also much higher than TP inputs measured in the inflowing streams (Trew et al. 1981). Unfortunately, monthly estimates of TP_r were not presented and a correct TP_r could not be used for the Ethel Lake budget. The effective drainage basin area (and thus runoff) is difficult to determine; it requires knowledge on whether the slope of the land is adequate for drainage and whether stream channels with beaver dams are "sufficiently" developed (Meid and Miller 1978). This detailed information is not available for the study lakes. Therefore, TP_r could not be corrected at the 15 lakes where there were no direct measurements. The overestimates of TP_r for these lakes could not explain the consistently positive values of TP_d.

TP sedimentation was low in early summer and increased to high in late summer and fall (Schindler et al. 1973). Also, TP sedimentation is greater in more productive lakes than in less productive lakes (Birch et al. 1980). Thus, a low and constant proportion (2%) of trophogenic TP_m was used to estimate sedimentation from this zone (TP_s). Expressed over A_0, average TP sedimentation over summer ranged from 1.4 $mg.m^{-2}.d^{-1}$ at Long Lake to 5 $mg.m^{-2}.d^{-1}$ at Baptiste Lake (Table 5.3). Average gross sedimentation in the study lakes of 2.6 $mg.m^{-2}.d^{-1}$ or $2\%.d^{-1}$ was less than reported in other studies (Table 5.7); for lakes with similar trophic status (i.e., [TP] in the trophogenic zone between 10 and 50 $mg.m^{-3}$), reported rates averaged 9.9 $mg.m^{-2}.d^{-1}$ and 2.7%. Thus, a

conservative estimate of TP_s was used in this study; the literature survey indicates that TP_s could be underestimated by 35 to 280%. It is extremely unlikely that the underestimated TP_s contributed to positive values of TP_d.

Loss of TP through the outflow (TP_o) may be overestimated in the study lakes, because runoff from the drainage basin is likely overestimated (as explained earlier). However, the overestimate of TP_o was by definition less than the overestimate of TP_r; most P entering the study lakes was retained there (R at all study lakes was greater than 0.65; Eq. 2). Thus, any overestimates of TP_o were offset by overestimates of TP_r; TP_o could not explain positive values of TP_d.

The budgets (with TP_r generally overestimated and TP_s likely underestimated) resulted in overestimates of $TP_{m,c}$ and thus in conservative (under)estimates of TP_d (Eq. 3). This bias towards low TP_d may explain the negative values of TP_d for Amisk and Twin lakes. The estimates of TP_d (Table 5.3) for the study lakes were similar to those found in epilimnetic budgets of two other stratified lakes: Shagawa and Mirror lakes with TP_d of 3.1 to 18, and 1.5 $mg.m^{-2}.d^{-1}$, respectively (Lie 1977; Caraco et al. 1988). P release from internal sources (i.e., hypolimnion or shallow sediments) is the mechanism that can most likely balance TP budgets in the trophogenic zone. This is not only the case in deep Alberta lakes, but also in a deep oligotrophic and another deep eutrophic lake (Mirror and Shagawa lakes, respectively).

P release from the hypolimnion

At eight lakes, rates of TP transport from the hypolimnion to the trophogenic zone could not account for TP_d (Table 5.4). At Lake 227, P released from the hypolimnion into the epilimnion was also insignificant

(Schindler et al. 1977). Discrepancies in short-term epilimnetic budgets for Shagawa and Mirror lakes could not be attibuted to TP transport from the hypolimnion to the trophogenic zone (Lie 1977: Caraco et al. 1988). Thus, TP transport from the hypolimnion into the trophogenic zone does not explain discrepancies in short-term TP budgets in either my study lakes or in Shagawa or Mirror lakes.

P release from shallow sediments

By process of elimination, P release from shallow sediments was the most likely source of P to balance my TP budgets. Porewater SRP is the most mobile P fraction in bottom sediments; it is the only fraction released into overlying lakewater (Bostrom et al. 1982). In most of my study lakes, porewater was sampled only once; at Baptiste and Narrow lakes, it was sampled twice. In shallow sediments, SRP gradients across the sediment-water interface increased 4% from May to August and 67% from May to June at Baptiste and Narrow lakes, respectively. These seasonal changes in SRP gradients at Baptiste and Narrow lakes were very small relative to the difference in SRP gradients between the study lakes (Table 5.6).

At the five lakes where porewater was collected, P release by molecular diffusion from shallow sediments was on average only 13% of TP_d calculated from short-term budgets. The diffusion coefficient used in Eq. 5 does not include P transport from sediments to lakewater by bioturbation, mixing, or groundwater flow. Transport of P by bioturbation and mixing are likely much more important than transport by molecular diffusion (e.g., Aller 1978; Gallepp 1979; Holdren and Armstrong 1980; Twinch and Peters 1984). Transport of P by groundwater may also be significant (Brock et al. 1982).

Macrophytes released P to the trophogenic zone of Shagawa Lake (Lie 1977). Since at least 70% of P in macrophytes originates from bottom sediments (Carignan and Kalff 1980), P release from macrophytes is indirectly from shallow sediments. However, release from healthy macrophytes is unlikely (Carignan and Kalff 1982). In addition, massive senescence of macrophytes in the study lakes does not occur before the last day of budget calculations (August 26). Thus, P release from macrophytes did not affect my TP budgets.

In this study, P release from shallow sediments by molecular diffusion is an underestimate of actual release. Since SRP gradients are present across the sediment-water interface at all five study lakes, mixing, bioturbation and groundwater flow enrich the trophogenic zone with TP.

In conclusion, this study presents evidence for the importance of P release from shallow sediments in several deep lakes. When Amisk and Twin lakes (with negative TP_d) were excluded, estimates of P release, based on TP_d, averaged 2.9 $mg.m^{-2}.d^{-1}$ (Table 5.3). On average, this potential release was greater than TP input either from atmospheric deposition (0.18 $mg.m^{-2}.d^{-1}$) or runoff from the watershed (2.11 $mg.m^{-2}.d^{-1}$, respectively). [TP] and the ratio of shallow sediment area (A_s) to A_0 ($A_s:A_0$) were significantly correlated with positive estimates of TP_d for these 14 lakes: df = 12, $\underline{r}^2$ = 0.48 and 0.46, respectively, $\underline{P} < 0.05$. Although the number of lakes (14) is very small, I performed a multiple regression of TP_d on both [TP] and $A_s:A_0$; it explained significantly more variance than [TP] and $A_s:A_0$ alone (Fig. 5.1; multiple regression: df = 2,11, $\underline{r}^2$ = 0.86, $\underline{P} < 0.01$; tests of significance: df = 1,11, $\underline{F}$ = 33.6 and 29.6, respectively, $\underline{P} < 0.001$;

Snedecor and Cochran 1980). Although more data are needed to support these tentative results, they are consistent with the conclusion on the potential importance of shallow sediment P release. Lake trophic status was positively correlated with mobile porewater P parameters (Chapter 4). In addition, calculated rates of sediment P release by molecular diffusion were correlated with exchangeable particulate P fractions (Chapter 3). Thus, the extent and mobile P content of shallow sediments may be important factors in balancing trophogenic TP budgets during summer and determining P release from shallow sediments.

Many potential errors could be associated with TP budgets. However, the underestimates of TP_s and overestimates of TP_r result in a conservative (low) estimate of TP_d for the study lakes. Conservative values of TP_d were positive when the study lakes were (naturally) eutrophic and/or were situated in relatively small drainage basins. In small, meso-eutrophic Twin Lake and eutrophic Amisk Lake (both with relatively large drainage basin areas) overestimates in TP_r likely overshadowed changes in TP_m. In addition, care must be taken to obtain accurate estimates of all P gains and losses in more oligotrophic lakes (as was done for Mirror Lake; Caraco et al. 1988). The results from this study may not extend to artificially eutrophied lakes; no net sediment P release (i.e., release - sedimentation) was observed at Lake 227 (Schindler et al. 1977). In artificially eutrophied lakes, lakewater is enriched relative to bottom sediments. This condition is similar to laboratory experiments where the P sorption capacity of sediments is determined. Under these artificial conditions (i.e., no equilibrium between P in sediment and water), sediments bind P strongly (Williams et al. 1970; Schindler et al. 1977). In artificially

eutrophied lakes, sediment P release may not occur at all, or only after lakewater P is drastically reduced (as in P desorption following sorption experiments; Williams et al. 1970).

This study shows that to predict P accurately in the trophogenic zone, a better understanding of the interactions between shallow sediments and lakewater is imperative. This knowledge will not only produce more complete P budgets for lakes, but also enable better predictions on the "recovery" of eutrophic lakes after implementation of management techniques aimed at P reduction.

5.6 REFERENCES

Aller, R. C. 1978. Experimental studies of changes produced by deposit feeders on porewater, sediment, and overlying water chemistry. Am. J. Sci. 278: 1185-1234.

Babin, J. 1984. Winter oxygen depletion in temperate zone lakes. MSc thesis, Univ. of Alta. 108p.

Bengtsson, L. 1975. Phosphorus release from a highly eutrophic lake sediment. Verh. Internat. Verein. Limnol. 19:1107-1116.

Berner, R. A. 1980. Early Diagenesis. Princeton Univ. Press, Princeton, N. J. 241p.

Birch, P. B., R. S. Barnes, and D. E. Spyridakis. 1980. Recent sedimentation and its relationship with primary productivity in four western Washington lakes. Limnol. Oceanogr. 25:240-247.

Bloesch, J., P. Stadelmann, and H. Buhrer. 1977. Primary production, mineralization, and sedimentation in the euphotic zone of two Swiss lakes. Limnol. Oceanogr. 22:511-526.

Bostrom, B., I. Ahlgren, and R. Bell. 1985. Internal nutrient loading in a eutrophic lake, reflected in seasonal variations of some sediment parameters. Verh. Internat. Verein. Limnol. 22:3335-3339.

Bostrom, B., M. Jansson, and C. Forsberg. 1982. Phosphorus release from lake sediments. Arch. Hydrobiol. 18:5-59.

Brock, T. D., D. R. Lee, D. Jones, and D. Winek. 1982. Groundwater seepage as a nutrient source to a drainage lake; Lake Mendota, Wisconsin. Water Res. 16:1255-1263.

Canfield, D. E. Jr., J. R. Jones, and R. W. Bachman. 1982. Sedimentary losses of phosphorus in some natural and artificial Iowa lakes.

Hydrobiologia 87:65-76.

Caraco, N. F., J. J. Cole, G. E. Likens, M. D. Mattson, and S. Nolan. 1988. A very imbalanced nutrient budget for Mirror Lake, New Hampshire, U.S.A. Verh. Internat. Verein. Limnol. 23:170-175.

Carignan, R. 1984. Interstitial water sampling by dialysis: methodological notes. Limnol. Oceanogr. 29:667-670.

Carignan, R., and J. Kalff. 1980. Phosphorus sources for aquatic weeds: water or sediments. Science 207:987-989.

Carignan, R., and J. Kalff. 1982. Phosphorus release by submerged macrophytes: significance to epiphyton and phytoplankton. Limnol. Oceanogr. 27:419-427.

Charlton, M. N. 1975. Sedimentation: measurements in experimental enclosures. Verh. Internat. Verein. Limnol. 19:267-272.

Dillon, P. J., and W. B. Kirchner. 1975. The effects of geology and land use on the export of phosphorus from watersheds. Water Res. 9:135-148.

Dillon, P. J., and F. H. Rigler. 1975. A simple method for predicting the capacity of a lake for development based on lake trophic status. J. Fish. Res. Board Can. 32:1519-1531.

Fee, E. J. 1979. A relation between lake morphometry and primary productivity and its use in interpreting whole-lake eutrophication experiments. Limnol. Oceanogr. 24:401-416.

Gachter, R. 1968. Phosphorhaushalt und planktische Primarproduktion im Vierwaldstattersee (Horwer Bucht). Schweiz. Z. Hydrol. 30:1-66.

Gallepp, G. W. 1979. Chironmid influence on phosphorus release in sediment-water microcosms. Ecology 60:547-556.

Green, R. 1972. Geological map of Alberta. Research Council of Alberta

map (scale 1:1,267,000).

Hesslein, R. H. 1976. An in situ sampler for close interval pore water studies. Limnol. Oceanogr. 21:912-914.

Holdren, G. C., and D. E. Armstrong. 1980. Factors influencing phosphorus release from intact lake sediment cores. Environ. Sci. Technol. 14: 79-87.

Kamp-Nielsen, L. 1975. A kinetic approach to the aerobic sediment-water exchange of phosphorus in Lake Esrom. Ecol. Model. 1:153-160.

Kjearsgaard, A. A. 1972. Soil Survey of Tawatinaw (83-I). Univ. Alta Bull., No. SS-12. 102p.

Kortmann, R. W., D. D. Henry, A. Kuether and S. Kaufman. 1982. Epilimnetic nutrient loading by metalimnetic erosion and resultant algal responses in Lake Waramaug, Connecticut. Hydrobiologia 92:501-510.

Lean, D. R. S., M. N. Charlton, B. K. Burnison, T. P. Murphy, S. E. Hillard, and K. R. Young. 1975. Phosphorus: changes in ecosystem metabolism from reduced loading. Verh. Internat. Verein. Limnol. 19:249-257.

Lie, G. B. 1977. Phosphorus cycling by freshwater macrophytes - the case of Shagawa Lake. Ph. D. thesis, University of Minnesota-Minneapolis, MN. 67p.

Meid, P. O., and G. T. Miller. 1978. Report on calculations of gross and effective drainage areas for the prairie provinces. Hydrology Memorandum #25. Engineering Service, Prairie Farm Rehabilitation Admin., Dep. Regional Economic Expansion. Regina, Saskatchewan. 41p.

Mitchell, P. 1985. Preservation of water quality in Lake Wabamun. Lake

Wabamun eutrophication study. Alta Environ., Water Quality Branch, Poll. Control Div., Edmonton, Alta. 26p.

Munn, N., and E. Prepas. 1986. Seasonal dynamics of phosphorus partitioning and export in two streams in Alberta, Canada. Can J. Fish. Aquat. Sci. 43:2464-2471.

Murphy, J., and J. P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27:31-36.

Ostrofsky, M. L. 1978. Modification of phosphorus retention models for use with lakes with low areal water loading. J. Fish. Res. Board Can. 35:1532-1536.

Prepas, E. E. 1983. The influence of phosphorus and zooplankton on chlorophyll levels in Alberta lakes. RMD Report 83/23, Research Management Div., Alta. Environ., Edmonton, Alta. 111p.

Quay, P. D., W. S. Broecker, R. H. Hesslein, and D. W. Schindler. 1980. Vertical diffusion rates determined by tritium tracer experiments in the thermocline and hypolimnion of two lakes. Limnol. Oceanogr. 25:201-218.

Quigley, M. A., and J. A. Robbins. 1986. Phosphorus release processes in nearshore southern Lake Michigan. Can. J. Fish. Aquat. Sci. 43:1201-1207.

Rigler, F. H. 1973. A dynamic view of the phosphorus cycle in lakes. p 539-572. In E. J. Griffith, A. Beeton, J. H. Spencer, and D. T. Mitchell (eds.). Environmental Phosphorus Handbook. John Wiley & Sons, New York, N.Y.

Rigler, F. H. 1974. Phosphorus cycling in lakes. p. 263-273. In F. Ruttner (ed.). Fundamentals of Limnology. 3rd ed. University of

Toronto Press, Toronto, Ont.

Schindler, D. W., R. Hesslein, and G. Kipphut. 1977. Interactions between sediments and overlying waters in natural oligotrophic and experimentally-eutrophied Precambrian Shield lakes. p. 235-243. In H. L. Golterman (ed.). Interactions between sediments and freshwater (Proc. S.I.L.-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands.

Schindler, D. W., H. Kling, R. V. Schmidt, J. Prokopowitz, V. E. Frost, R. A. Reid, and M. Capel. 1973. Eutrophication of Lake 227 by the addition of phosphate and nitrate: the second, third, and fourth years of enrichment, 1970, 1971, and 1972. J. Fish. Res. Board Can. 30:1415-1440.

Schindler, D. W., T. Ruszczynski, and E. J. Fee. 1980. Hypolimnion injection of nutrient effluents as a method for reducing eutrophication. Can. J. Fish. Aquat. Sci. 37:320-327.

Shaw, R. D., A. M. Trimbee, A. Minty, H. Fricker, and E. E. Prepas. 1989. Atmospheric deposition of phosphorus and nitrogen in central Alberta with emphasis on Narrow Lake. Water, Air and Soil Pollut. 42. In press.

Snedecor, G. W., and W. G. Cochran. 1980. Statistical Methods. 7th ed. The Iowa State University Press, Ames, IA. 507p.

Sokal, R. R., and F. J. Rohlf. 1981. Biometry. 2nd ed. Freeman, San Francisco, CA. 859p.

Stadelmann, P., and A. Fraser. 1974. Phosphorus and nitrogen cycle on a transect in Lake Ontario during the International Field Year 1972-1973. p. 92-108. In Proceedings of the 17th Conference on Great Lakes Research, Ann Arbor, MI.

Stauffer, R. E. 1987. Vertical nutrient transport and its effect on epilimnetic phosphorus in four calcareous lakes. Hydrobiologia 154:87-102.

Stauffer, R. E., and D. E. Armstrong. 1984. Lake mixing and its relationship to epilimnetic phosphorus in Shagawa Lake, Minnesota. Can. J. Fish. Aquat. Sci. 41:57-69.

Trew, D. O., D. J. Beliveau, and E. I. Yonge. 1987. The Baptiste Lake Study. Technical Report. Alta. Environ., Water Quality Control Branch, Poll. Control Div., Edmonton, Alta. 380p.

Trew, D. O., E. I. Yonge, and R. P. Kaminski. 1981. A preliminary trophic assessment of nine lakes in the Cold Lake region. Alta. Environ., Water Quality Control Branch, Poll. Control Div., Edmonton, Alta. 70p.

Twinch, A. J., and R. H. Peters. 1984. Phosphate exchange between littoral sediments and overlying water in an oligotrophic north-temperate lake. Can. J. Fish. Aquat. Sci. 41:1609-1617.

Vollenweider, R. A. 1976. Rotsee, a source, not a sink for phosphorus? A comment and a plea for nutrient balance studies. Hydrobiologia 38:29-34.

Wetzel, R. G. 1983. Limnology. 2nd ed. Saunders, Philadelphia, PA. 767p.

Williams, J. D. H, J. K. Syers, R. F. Harris, and D. E. Armstrong. 1970. Adsorption and desorption of inorganic phosphorus by lake sediments in a 0.1 M NaCl system. Environ. Sci. Technol. 4:517-519.

Table 5.1. Location, surface area (A_0 in km^2), average depth (z in m), depth of trophogenic zone (z_{mix}), ratio of shallow sediments (A_s) to A_0 ($A_s:A_0$ in %), volume of water above z_{mix} (V_{mix} in dam^3), drainage basin size (A_d in km^2) and mean summer trophogenic total phosphorus (TP in $mg.m^{-3}$) of 16 study lakes in central Alberta.

Lake	Location		A_0	z	z_{mix}	$A_s:A_0$	V_{mix}	A_d	TP
	^oN	^oW							
Amisk[1,2]	54° 35'	112° 37'	4.2	16	6	30	20959	244	37
Baptiste South[1,2,3]	54° 45'	113° 33'	4.6	13	5	31	19909	179	49
Bourque[3]	54° 40'	110° 33'	5	8	8	50	30535	113	18
Eden[1,2]	53° 35'	114° 09'	0.2	6	9	61	965	2	20
Ethel[3]	54° 31'	110° 21'	4.8	7	8	69	22902	537	19
Hilda[3]	54° 31'	110° 25'	3.6	6	7	49	17514	79	22
Island North[2]	54° 52'	113° 31'	1.0	7	9	63	27787	7	20
Long[2]	54° 34'	113° 38'	1.6	9	10	63	10639	23	13
Marie[3]	54° 36'	110° 17'	36	14	9	25	273340	384	14
Minnie[3]	54° 17'	111° 07'	0.8	8	9	51	5319	5	32
Moore[3]	54° 31'	110° 29'	9.3	8	9	64	58782	33	23
Narrow[2]	54° 35'	113° 37'	1.1	14	12	47	10593	7	12
Peanut[1,2]	54° 01'	114° 21'	0.2	6	8	82	1147	1	25
Sauer[1,2]	53° 35'	114° 05'	0.1	4	8	85	321	1	28
Touchwood[3]	54° 49'	111° 24'	28	15	12	45	241878	111	21
Twin[1,2]	52° 55'	114° 20'	0.2	16	6	30	1192	5	18

References: [1]Babin 1984, [2]E. E. Prepas, unpubl. data, [3]D. O. Trew, Water Quality Control Branch, Alberta Environment, Edmonton, Alta, unpubl. data.

Table 5.2. Daily inputs of total phosphorus by atmospheric deposition to lakes during the summer of 1984 to 1986, estimated from monthly deposition rates determined at Narrow Lake, Alberta (from Shaw et al. 1989).

	Atmospheric deposition ($mg.m^{-2}.d^{-1}$)			
Month	1984	1985	1986	Average
May	0.229	0.210	0.281	0.239
June	0.110	0.117	0.203	0.143
July	0.129	0.100	0.103	0.110
August	0.084	0.087	0.116	0.097

Table 5.3. Estimates of total phosphorus (TP) missing in the trophogenic zone (TP_d) of 16 study lakes in central Alberta. TP_d is the difference between TP mass observed and estimated from TP budgets, expressed as a daily rate ($mg.m^{-2}.d^{-1}$) over lake surface area (A_0). Also indicated is the average sedimentation rate from the trophogenic zone over summer (2 % of TP mass), expressed as a daily rate over A_0 ($mg.m^{-2}.d^{-1}$). Mean and one standard error (SE) of TP_d and P sedimentation are presented where TP budgets were calculated for several years.

Lake	Year	TP_d mean	SE	P sedimentation mean	SE
Amisk	1980-82,87	-1.2	1.1	3.7	0.2
Baptiste	1980-84,86,87	11.3	1.7	3.5	0.3
Bourque	1981	0.7		2.2	
Eden	1982	1.1		2.3	
Ethel	1981-84,86,87	0.9	0.2	1.9	0.1
Hilda	1981	2.1		2.4	
Island	1986	2.5		2.2	
Long	1984,86	1.6	0.2	1.5	0.1
Marie	1981	4.9		2.0	
Minnie	1986	4.1		3.7	
Moore	1981	2.4		2.7	
Narrow	1980,83-87	3.2	0.2	2.0	0.1
Peanut	1982	1.5		2.2	
Sauer	1982	0.7		1.9	
Touchwood	1986	3.3		3.2	
Twin	1982	-3.8		2.0	

Table 5.4. Estimated transport of total phosphorus (TP) into the trophogenic zone of eight Alberta lakes: (1) by eddy diffusion calculated with average summer TP gradients from the hypolimnion into the trophogenic zone for the year indicated (hypolimnion), and (2) from discrepancies between the TP mass observed and estimated with trophogenic TP budgets (TP_d) during the same years as (1). Both are daily rates expressed over lake surface area.

Lake	Year	Gradient	P release in $mg.m^{-2}.d^{-1}$	
		$mg.m^{-4}$	hypolimnion	TP_d
Amisk	1980-81	11.0	0.05	0.6
Baptiste	1980-82	1.9	0.01	10.9
Eden	1982	12.1	0.03	1.1
Island	1986	18.4	0.05	2.5
Long	1986	0.2	0.01	1.2
Narrow	1980,83-87	0.04	0.003	3.2
Peanut	1982	6.7	0.01	1.5
Sauer	1982	-14.3	0	0.7

Table 5.5. Soluble reactive phosphorus (SRP) concentrations (in $mg.m^{-3}$) above and below the sediment-water interface, gradients ($mg.m^{-4}$) across this interface, and water content of sediments 0 to 2 cm below this interface (by weight, %POR) at five study lakes in central Alberta. For each lake, data from three to four depths (m) are presented as is the proportion of shallow sediments represented by each depth (Weight).

Lake	Date	Depth	SRP			%POR	Weight
			above	below	gradient		
Baptiste	May 20/22	2.5	13	148	9000	37	0.418
		4	17	206	12600	36*	0.457
		5	24	286	17470	33	0.125
	August 17	2.5	8	67	3933		
		4	18	197	11933		
		5	15	621	40400		
Island	June 10/11	2.5	4	124	8000	25	0.524
		4	8	185	11800	30	0.173
		5	4	74	4670	51	0.173
		7.5	21	43	1470	96	0.130
Long	June 4/5	2.5	2	173	11400	90	0.325
		4	2	11	600	95	0.242
		5	8	80	4800	94	0.433
Minnie	July 15	2.5	17	29	800	95	0.415
		5	50	1232	78800	94	0.356
		7.5	7	166	10600	93	0.229
Narrow	May 24/25	2.5	6	86	5330	52	0.206
		5	6	14	530	47	0.234
		7.5	7	14	470	29	0.285
		10	5	31	1730	39	0.275
	June 23	2.5	6	75	4600		
		5	6	19	867		
		7.5	8	17	600		
		10	7	102	6333		

* estimated

Table 5.6. Diffusion rates (J in $mg.m^{-1}.d^{-1}$) calculated from soluble reactive phosphorus gradients across the sediment-water interface. Rates are expressed over the entire lake surface area for five study lakes in central Alberta. The gradients ($mg.m^{-4}$) and water content (ϕ by volume) were pooled for two to four depths and weighted by area (Table 5.5). Tortuosity (θ^2) was calculated from water content ($\phi^{-0.8}$; Berner 1980). Also indicated are estimated phosphorus release rates calculated from differences between TP observed and estimated with short-term budgets in 1986 (TP_d in $mg.m^{-2}.d^{-1}$).

Lake		Gradient	ϕ	θ^2	J	TP_d
Baptiste	May	11700	0.43	1.96	0.09	6.8
	August	12147	"	"	0.09	"
Island		7230	0.47	1.82	0.13	2.5
Long		5930	0.93	1.06	0.35	1.7
Minnie		30810	0.94	1.05	1.50	4.1
Narrow	May	1830	0.49	1.78	0.03	3.6
	June	3063	"	"	0.09	"

Table 5.7. Published sedimentation rates (TP_s) of total phosphorus (TP) from the trophogenic zone during summer stratification for several lakes. Concentrations of TP in the trophogenic zone are indicated for most lakes ([TP] in $mg.m^{-3}$).

Lake	[TP]	TP_s		Reference
		$mg.m^{-2}.d^{-1}$	%	
Mendota	37		5.6	Stauffer 1987
Delavan	76		4.0	"
Lake 227	38		3.2	Schindler et al. 1973
Toussaint			1.0	Rigler 1973
Linsley Pond	21		2.0	"
Lucerne	12 - 45		2.0	Gachter 1968
"		4.4		Bloesch et al. 1977
Rotsee	36 - 94	7.0		"
West Okoboji	19	13.3		Canfield 1982
Spirit	40	20.8		"
East Okoboji	139	60.3		"
Lost Island	110	218		"
Mirror	6	1.5		Caraco et al. 1988
Shagawa	27	2.2-17		Lie 1977
Ontario-main basin	19	1.6		Stadelmann and Fraser 1974
-Bay of Quinte	38		2.5	Lean et al. 1975
"			2.9	Charlton 1975

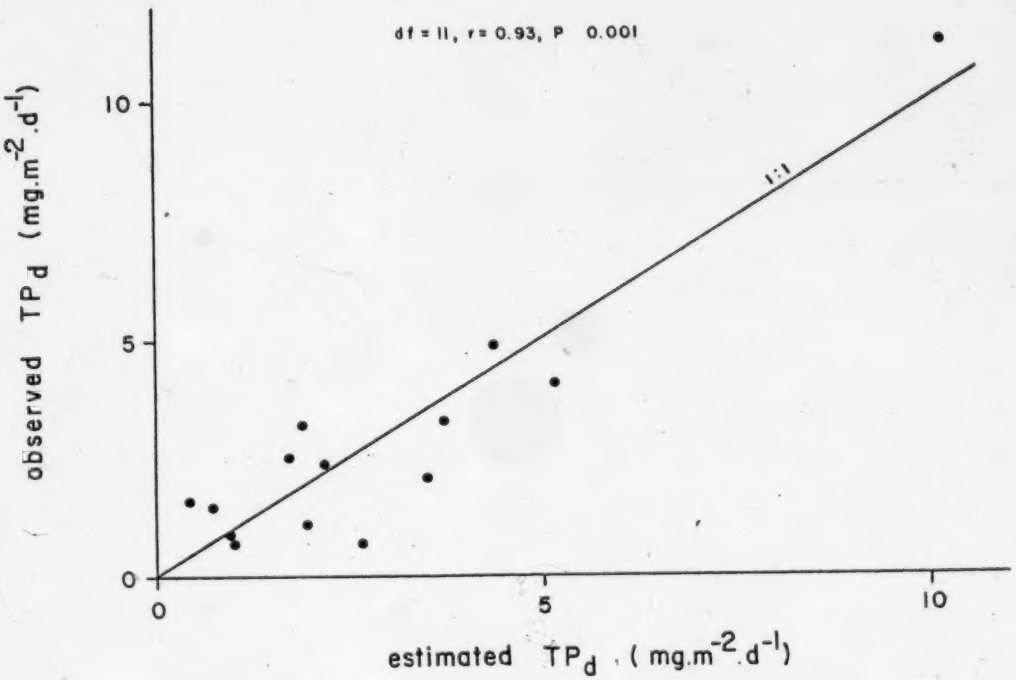

Fig. 5.1. Relationship between observed TP_d and TP_d estimated from [TP] in the trophogenic zone ($[TP]_{troph}$) and portion of shallow sediments in the lakes ($\%A_s$) with multiple regression analyses:
($TP_d = 4.3156 + 0.1842 * [TP]_{troph} - 0.0999 \% A_s$)

6. GROUNDWATER TRANSPORT OF PHOSPHORUS FROM LAKE BOTTOM SEDIMENTS INTO LAKEWATER

6.1 ABSTRACT

Phosphorus (P) is the nutrient that limits algal biomass in most lakes. Lake bottom sediments are rich in P; even so, advective transport of P by groundwater to lakewater is rarely measured. In this study, simple methods were used to estimate in situ rates of advective transport of P to six lakes in western Canada. In general, input of P from anaerobic sediment porewater to aerobic lakewater was not inhibited by sorption onto iron- or calcium-complexes. Advective transport of P to the lakes averaged 180, 30, and 240% of P inputs from molecular diffusion, surface runoff and atmospheric deposition, respectively.

6.2 STUDY

Phosphorus (P) is the nutrient that limits algal production in most lakes (1); thus, much effort has been directed to quantify sources of P to lakes. Lake bottom sediments contain a vast pool of P, and groundwater flowing into lakes may transport P from sediment porewater into the overlying lakewater. However, advective transport of P by groundwater into lakes has been largely ignored, probably because of perceived difficulties in measuring groundwater-lake flux (2). In addition, P release from anaerobic porewater into aerobic lakewater is thought to be unlikely due to sorption of P onto iron- or calcium-complexes (3,4). In this study I demonstrate that (i) simple methods

can be used to quantify advective transport of P from sediments to lakewater, (ii) P influx from anaerobic porewater to aerobic lakewater is possible and (iii) advective transport of P was important relative to other P inputs to six north-temperate lakes in western Canada.

The six study lakes are of glacial origin and are located in central Alberta (Table 6.1). Glacial till is the predominant surficial deposit; it is underlain by sedimentary bedrock. Surface area and maximum depth of the study lakes varied from 1.1 to 9.2 km^2 and from 7 to 36 m, respectively; trophic status ranged from meso-eutrophic to eutrophic (Table 6.1). Morphometry and trophic status of the study lakes are representative of other lakes in the region (5).

During the study period (May to July, 1986), water in Tucker Lake was isothermal. The other lakes were thermally stratified; thus, P inputs to the lakes from hypolimnetic sediments were trapped below the thermocline (6). In contrast, P input to lakes from shallow sediments (7) enters surface waters directly, and thus is more likely to be utilized by algae. In addition, groundwater seepage into lakes is generally concentrated near shore (8). Therefore, the focus of this study was on advective transport of P from shallow sediments into lakewater.

The rate of P influx by groundwater was determined along one transect in each study lake. At five lakes, transects extended perpendicular from shore to the edge of the shallow sediments; at Tucker Lake, the transect extended from shore to 100 m from shore (Table 6.1). The location of the transect within each lake was selected to represent the average slope of the bottom sediments (i.e., ratio of distance from shore to lake depth). Groundwater seepage rates were measured <u>in situ</u>

with seepage meters (9) at 4 to 10 sites along each transect. Based on seepage meter data, an average seepage rate along each transect was computed which was weighted for distance from shore. A jackknife technique was used to reduce bias and provide an estimate of variance for our estimates of average seepage rates (10). Within 24 h of sampling seepage meters, sediment porewater was collected with peepers (11) at two to nine sites along each transect. Porewater was analyzed for soluble reactive P (SRP), Fe^{2+}, and pH (12). Porewater SRP and Fe^{2+} were assumed to be the P and Fe (13) fractions, respectively, in sediment porewater that could be transported by groundwater to overlying lakewater. At five lakes seepage rates and porewater SRP concentrations were measured once from 20 May to 21 July, 1986; at Narrow Lake they were measured twice (24 May and 23 June, 1986). The rate of advective transport of P along each transect was computed from the average seepage rate and average porewater SRP concentration (14).

Seepage rates into the study lakes (10^{-10} to 10^{-8} $m.s^{-1}$) were within the range measured with seepage meters at other lakes in Canada, United States, and New Zealand (15). At two seepage meter sites in Narrow Lake (24 May 1986) and one site in Tucker Lake there was no seepage flux; at another site in Tucker Lake, seepage was from the lake to the groundwater system (10^{-9} $m.s^{-1}$). Average seepage rates along the transects varied 3-fold between the study lakes (Table 6.2). Except for transects at Baptiste and Jenkins lakes, seepage rates decreased significantly ($P<0.05$) with distance from shore (10). The predominance of (i) measured nearshore seepage flux into lakes, and (ii) observed patterns of decreased seepage offshore are consistent with hypotheses generated from computer simulation modeling of hypothetical groundwater-

lake systems (7).

Porewater SRP concentrations in the study lakes (29 to 2274 $mg.m^{-3}$) were within the range measured in porewater of shallow sediments at other lakes in Canada, United States, England and Sweden (16). The range of porewater Fe^{2+} concentrations in the study lakes (65 to 1954 $mg.m^{-3}$) was of similar magnitude as SRP concentrations, and porewater pH ranged from 7.5 to 9.0 (Table 6.2). Average porewater SRP concentrations along the transects varied 31-fold between lakes. Unlike seepage rates, there was no distinct pattern of porewater SRP concentrations with distance from shore.

Phosphorus is reactive. Under aerobic conditions and if a minimum molar ratio of Fe:P of 1.8 is exceeded most P sorbs onto iron oxy-hydroxides (3). The formation of these iron-phosphorus complexes would prevent influx of P from anaerobic porewater to aerobic lakewater. However, porewater from the study lakes had an average Fe:P molar ratio of 0.9, and the critical value (1.8) was exceeded at only 4 of 20 peeper sites. At pH greater than 8, P can sorb onto calcium-carbonates, and sorption increases with increasing pH (4). However, porewater pH at all lakes but Tucker Lake was 8 or less; at Tucker it was 9.0 (Table 6.2). Therefore, at most sites in the study lakes influx of P from porewater to lakewater was possible.

Rates of advective transport of P along the transects varied two-orders of magnitude from 0.05 to 3.1 $mg.m^{-2}.d^{-1}$ (Table 6.2); there was no significant difference between rates of advective transport of P into Narrow Lake for May and June 1986 (t=0.85, df=13, P>0.40; 17). Therefore, methods used in this paper can give reproducible estimates of P inputs to lakes by groundwater. Expressed over the surface area of

the entire lake, P inputs from groundwater flowing through shallow sediments ranged from 0.02 to 1.58 $mg.m^{-2}.d^{-1}$ (Table 6.3). Within a single lake, seepage rates and porewater P concentrations may vary temporally and spatially (2,15,16). Therefore, the estimates of advective transport of P into the study lakes should be considered preliminary values. For improved estimates of inputs of P from groundwater to a single lake transects should be sampled (i) at regular time intervals over the course of a study, and (ii) at several locations in a lake.

Phosphorus inputs from groundwater to Lake Mendota, WI, were estimated with comparable methods to those in this study (2). Interestingly, the rate of advective P transport to Lake Mendota (0.31 $mg.m^{-2}.d^{-1}$) was similar to the average rate into our study lakes (0.43 $mg.m^{-2}.d^{-1}$). Other studies have estimated groundwater P inputs to lakes based on P concentrations measured in nearby water wells (18). Those water samples may be adequate for estimating inputs of conservative solutes into lakes (19), but are likely not representative of non-conservative solutes. For example, P concentrations in porewater at Narrow Lake were, on average, 440% of P concentrations measured in wells near the lake (20). To accurately estimate advective transport of P (or other non-conservative solutes) to lakes, samples should be collected as close as possible to the point of effluent discharge into the lake (i.e., sediment-water interface).

In addition to groundwater, solutes can also be transported from porewater to lakewater by molecular diffusion, bioturbation, and physical mixing. It is difficult to quantify P influx due to bioturbation or physical mixing. However, rates of molecular diffusion

of P from shallow sediments to the study lakes were previously determined (21); loading rates of P by advective transport were, on average, 180% of molecular diffusion rates. Influx of P from groundwater to the study lakes was, on average, 30 to 220% of P input from surface runoff and inputs from atmospheric deposition, respectively (Table 6.3; Chapter 5). Thus, relative to other internal and external sources of P, groundwater transport was an important source of P to the surface waters of the six study lakes.

Methods used in this study can be applied to measure advective transport of both conservative and non-conservative material to lakes. Although groundwater flow rates into lakes situated in glacial till are low (10), this study demonstrates that groundwater can be a major source of P to these lakes. Groundwater inputs should not be overlooked when preparing nutrient budgets for lakes.

6.3 REFERENCES AND NOTES

1. D. W. Schindler, Science 195, 260 (1977).
2. T. D. Brock, D. R. Lee, D. Jones, D. Winek, Water Res. 16, 1255 (1982).
3. U. Tessenow, Arch. Hydrobiol. Suppl. 47, 1 (1974).
4. A. Otsuki, R. G. Wetzel, Limnol. Oceanogr. 17, 763 (1972).
5. E. E. Prepas, D. O. Trew, Can. J. Fish. Aquat. Sci. 40, 27 (1983).
6. D. W. Schindler, R. Ruszczynski, E. J. Fee, Can. J. Fish. Aquat. Sci. 37, 320 (1980).
7. Shallow sediments were defined as those in contact with water in the euphotic zone or epilimnion, whichever was deeper. In the study lakes, the proportion of shallow sediments to lake area varied from 47 to 100 % (Table 6.1).
8. T. C. Winter, U. S. Geol. Surv. Prof. Pap. 1001 (1976).
9. Seepage rates were determined by enclosing an area of lake bottom with a cylinder (i.e., seepage meter) that was vented to a plastic bag. The cylinder was constructed by cutting the top 20-cm of a "45-gallon" drum (diameter = 57 cm) as described by D.R. Lee, Limnol. Oceanogr. 22, 140 (1977). Seepage rates were computed from the volume of water collected in the bag after appropriate corrections for anomalous short-term influx of water in bag, area of bottom enclosed by the cylinder and sampling interval (10).
10. R. R. Sokal, F. J. Rohlf, Biometry, Freeman, San Francisco, 2nd ed. (1981); R. D. Shaw, E. E. Prepas, manuscript in prep.
11. Peepers are dialysis chambers which collected porewater 0-10 cm below the sediment-water interface as described by R. Hesslein,

Limnol. Oceanogr. 21, 912 (1976).

12. Porewater collection: Chapter3; porewater analyses: J. Murphy, J. P. Riley, Anal. Chim. Acta 27, 31 (1962); American Public Health Association, Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPFC, New York, 15th ed. (1980)

13. R. G. Carlton, R. G. Wetzel (Limnol. Oceanogr. 33, 562 [1988]) report that oxygen penetration into sediments is limited to < 4mm below the sediment-water interface. Therefore, we assumed porewater 0-10 cm below the sediment-water interface was anaerobic; thus, all Fe in porewater would be Fe^{2+}. Sorption onto particulate Fe^{3+} in aerobic porewater near the sediment surface may not be important due to intense mixing of porewater with lakewater: R. Carignan, A. Tessier, Science 228, 1524 (1985).

14. Average seepage rate (q^*, in log-$m.d^{-1}$) and porewater P concentration (P^*, in log-$mg.m^{-3}$) along each transect were calculated from $\log_{10}$-transformed data (10,21). Therefore, the average rate of advective transport of P along a transect (L, $mg.m^{-2}.d^{-1}$) was estimated from: $L = 10^{L^*}$, where $L^* = q^* + P^*$. The variance of L^* (V_{L^*}) was computed from $V_{L^*} = V_{q^*} + V_{P^*}$.

15. D. R. Lee, Limnol. Oceanogr. 22, 140 (1977); J. A. Downing, J. J. Peterka, Limnol. Oceanogr. 23, 821 (1978); M. A. Lock, P. H. John, Int. Rev. ges. Hydrobiol. 63, 271 (1978); C. R. Fellow, R. L. Brezonik, Wat. Res. Bull. 16, 635 (1980); J. N. Connor, T. V. Belanger, Wat. Res. Bull. 17, 799 (1981).

16. G. C. Holdren, D. E. Armstrong, R. F. Harris, Water Res. 11, 1041 (1977); W. Ripl, G. Lindmark, Arch. Hydrobiol. 86, 45 (1979); R. Carignan, Verh. Int. Verein. Limnol. 22, 355 (1984); J. C. Drake,

S. I. Heany, Freshwater Biol. 17, 513 (1987).

17. t-test of the difference between two means according to R. R. Sokal, F. J. Rohlf, Biometry (W.H. Freeman and Co., San Fransisco, 1981).

18. e.g., P. A. Mitchell, Preservation of water quality in Lake Wabamun, Alberta Environment, Edmonton (1985); D. O. Trew, D. J. Beliveau, E. I. Yonge, The Baptiste Lake Report, Alberta Environment, Edmonton (1987).

19. J. P. Hurley, D. E. Armstrong, G. J. Kenoyer, C. J. Bowser, Science 227, 1576 (1985).

20. Total P concentrations in groundwater, collected from wells near the transect site at Narrow Lake, ranged from 18 to 27 $mg.m^{-3}$ (mean = 23 $mg.m^{-3}$).

21. Chapter 5.

22. During May to August 1986, P influx to the lakes from surface runoff and atmospheric deposition averaged 1.29 and 0.18 $mg.m^{-2}.d^{-1}$, respectively (21).

Table 6.1. Location, surface area (A_o in km^2), maximum depth (z_{max} in m), mean summer trophogenic total phosphorus (TP in $mg.m^{-3}$), ratio of shallow sediments (A_s) to lake surface area, and transect length (TL in m) of the six study lakes.

Lake	Location N	Location W	A_o	z_{max}	TP	$A_s:A_o$	TL
Baptiste	54° 45'	113° 33'	9.2	26	38	0.63	60
Island	54° 52'	113° 31'	7.8	15	20	0.93	50
Jenkins	54° 55'	113° 36'	1.8	18	25	0.51	32
Long	54° 34'	113° 38'	1.6	28	13	0.69	40
Narrow	54° 35'	113° 37'	1.1	36	11	0.47	50
Tucker	54° 32'	110° 37'	7.2	7	42	1.00	100

Table 6.2. Groundwater flow rates, porewater soluble reactive phosphorus (SRP) concentrations and rates of advective P transport along the transects: mean and 95 % confidence intervals (in brackets). Also indicated are average pH and ferrous iron concentrations in porewater along the transects.

Lake	Groundwater	Porewater SRP	Advective Transport	pH	Fe
	$x10^{-8}$ $m.s^{-1}$	$mg.m^{-3}$	$mg.m^{-2}.d^{-1}$		$mg.m^{-3}$
Baptiste	2.07 (1.55-2.76)	415 (250-690)	0.74 (0.5-1.1)	7.9	247
Island	0.86 (0.56-1.33)	225 (115-442)	0.17 (0.1-0.3)	8.0	232
Jenkins	1.72 (0.14-20.9)	2113 (824-5420)	3.1 (0.1-15.6)	8.0	379
Long	0.65 (0.22-1.93)	230 (65-817)	0.18 (0.01-2.9)	7.9	945
Narrow May	1.05 (0.71-1.56)	57 (19-175)	0.05 (0.02-0.16)	7.8	250
June	0.80 (0.62-1.02)	144 (68-303)	0.10 (0.05-0.21)	-	-
Tucker	0.69 (0.34-1.42)	348 (168-720)	0.21 (0.10-0.41)	9.0	168

Table 6.3. Comparison of phosphorus (P) release rates by internal (advective transport and molecular diffusion) and external (runoff and atmospheric deposition) sources for the six study lakes. Rates are expressed as $mg.m^{-2}.d^{-1}$ over the entire lake surface.

	Internal		External	
Lake	Advective Transport	Molecular Diffusion	Runoff	Atmospheric Deposition
Baptiste	0.47	0.09	1.33	0.18
Island	0.16	0.13	0.61	0.18
Jenkins	1.58	0.52	2.00	0.18
Long	0.12	0.35	0.85	0.18
Narrow May	0.02	0.03	0.49	0.18
June	0.05	0.09	0.49	0.18
Tucker	0.21	0.30	2.46	0.18

7. GENERAL DISCUSSION

Although phosphorus (P) release from sediments into aerobic water may occur in laboratory core incubations, its significance to lakes is uncertain (e.g., Tessenow 1974; Davis et al. 1975; Wetzel 1983; Stauffer and Armstrong 1984; Stauffer 1987). In this study, I investigated potential P release from shallow sediments (i.e., those located in the trophogenic zone) into aerobic lakewater. The impact of P released from shallow sediments on water and biota in the trophogenic zone is immediate; during summer, this released P may stimulate algal growth. In addition, P release from sediments is temperature dependent and is likely mediated by biological activity (decomposition and bioturbation; Kamp-Nielsen 1975; Gallepp 1979). Thus, P release from shallow sediments would be greater during summer than during winter. Sediment P release into anaerobic hypolimnetic water may be high (e.g., Nurnberg 1988). During the summer, however, P released into either an aerobic or anaerobic hypolimnion (1) is contained below the thermocline due to density gradients across the thermocline, and (2) rarely affects the trophogenic zone (Stauffer and Armstrong 1984). Consequently, shallow sediments may be a significant P source for the trophogenic zone of many lakes during summer.

Measurement of P release from shallow sediments

Direct measurement of P release from shallow sediments is difficult. Any instrument (i.e., sediment cores, seepage meters, bell jars) used to trap released P from shallow sediments may affect *in situ* transport: (1) mixing and groundwater flow during these incubations decrease compared to *in situ* conditions, and (2) bioturbation and

molecular diffusion may decrease (due to decreased P gradients across the sediment-water interface without mixing in overlying lakewater in these devices). In addition, water enclosed by these instruments may become anaerobic during employment of the instuments. Under these conditions, release rates of P may be higher than under in situ conditions (Belanger and Mikutel 1985). Since direct measurements are problematic, I identify three indirect approaches to measure P release from sediments. These approaches are based on:

1) changes in P fractions of particulate sediments over time,
2) P gradients across the sediment-water interface, and
3) changes in lakewater P over time.

Changes in particulate P fractions

Nurnberg (1988) determined with core incubations in the laboratory that a decrease of exchangeable particulate P fractions was correlated with an increase of P in overlying water. The increase of P in overlying water was only 10 % of the P loss of one exchangeable P fraction (Nurnberg 1988). Since P is exchanged between different sediment P fractions (Bostrom 1984; Tiren and Pettersson 1985), monitoring one fraction may not be sufficient to establish P exchange from particulate to soluble fractions. In addition, the amount of P in particulate P fractions is much larger than present in overlying water (Bostrom et al. 1982); changes of P in overlying water are much easier to detect than the decrease in a particulate P fraction. For example: in a sediment core incubation (10 cm sediment, 50 cm water, diameter core 6 cm, water content sediment 95 %, exchangeable sediment P 100 $ug.g^{-1}$ dry weight, density 1.1 $g.cm^{-3}$), a 5 % decrease in exchangeable P (i.e., 5 $ug.g^{-1}$) would result in a dramatic increase of 111 $mg.m^{-3}$ in

overlying water. Thus, relative changes in particulate P fractions are much smaller than in overlying water and more difficult to determine accurately.

Changes of particulate P fractions due to P release from lake sediments have been determined in situ (Bengtsson 1975; Jacoby et al. 1982; Bostrom et al. 1985). However, P in particulate fractions varies with lake depth (Frink 1969); for example, CDB-P in the top 10 cm of the sediment at 7.5-m lake depth was 18 times the concentration at 2.5-m depth at Island Lake (Chapter 4). Thus, extrapolation of changes in particulate P fractions from few sites to the entire lake is difficult. In addition, particulate sediments are not an isolated compartment: (1) sedimentation continuously adds P to shallow sediments (however, this addition is difficult to measure; Bengtsson 1975), (2) transformations between various particulate P fractions are complex (Bostrom 1984; Tiren and Pettersson 1985), and (3) P exchange with deeper sediments may be possible (Nurnberg 1988). Since changes in particulate P fractions near the sediment surface may not be caused by P release from sediments alone, these changes were not used to estimate sediment P release in this study. Instead, I focussed on the remaining two approaches to estimate P release from shallow sediments indirectly.

P gradients across the sediment-water interface

In general, P gradients concentrations from porewater to lakewater indicate that sediment P release into lakewater is possible. In this study, P concentrations were greater in porewater than in lakewater just above shallow sediments at all but one site in nine study lakes (Chapter 3). SRP gradients in the eutrophic study lakes (excluding Figure Eight Lake) were similar to those reported in the literature (Table 7.1). The

gradients in the study lakes indicate that P transport by molecular diffusion or bioturbation (which includes excretion, respiration currents, physical mixing by benthic invertebrates) could enhance P concentrations in lakewater. In addition, movement of porewater (with P) into lakewater by groundwater flow or physical mixing (due to wind activity without resuspension of particulate sediments) could also increase lakewater P concentrations. These potential avenues of P release can only be realized if release is not hindered by precipitation or sorption, and the porewater P pool is replenished from other compartments.

Precipitation or sorption of P in porewater would inhibit its transport to lakewater. The general perception is that P is not released from sediments into aerobic lakewater due to P precipitation as hydroxyapatite and sorption onto ferric iron oxy-hydroxides (e.g., Wetzel 1983). In addition, vivianite precipitation could limit P release from anaerobic sediment sections. Precipitation or sorption of P was investigated in all nine study lakes.

Under anaerobic conditions, vivianite ($Fe_3(PO_4)_2.8H_2O$) may precipitate in porewater (e.g., Nriagu and Dell 1974; Tessenow 1974). The precipitation of vivianite depends on the activity of Fe^{2+}, PO_4^{-3}, and H^+. Based on the assumption that ferrous iron and SRP concentrations in the analyses are equal to Fe^{2+} and $H_2PO_4^-/HPO_4^{2-}$ concentrations, ion activity products (IAP) were calculated (Stumm and Morgan 1981). IAP were higher than the equilibrium activity product at several sites (Table 7.2); thus, vivianite precipitation was theoretically possible.

However, the analyses used in this study may overestimate Fe^{2+} and

$H_2PO_4^-/HPO_4^{2-}$; thus, IAP may have been overestimated. Ferrous iron could be present as $Fe(OH)^+$ or bound to organic colloids rather than as Fe^{2+}. At the pH measured in porewater of the study lakes, ratios of $Fe(OH)^+$ to Fe^{2+} varied from 0.01 to 1.37 (Table 7.2). Although porewater Fe^{2+} in the study lakes may have been overestimated by as much as 42%, IAP for vivianite were affected very little by a correction for $Fe(OH)^+$ (Table 7.2).

Due to acid hydrolysis during the iron and P analyses, small organic colloids may have dissolved and increased actual concentrations of Fe^{2+} and phosphate (Gjessing 1964; Lean 1973; Stainton 1980; McKnight et al. 1988). For example, SRP may overestimate inorganic P concentrations by a factor of 10 to 100 (Rigler 1966). If this range of SRP to inorganic phosphate ratios is correct, IAP in the study lakes (Table 7.2) would be overestimated by 100 to 10,000 times, and vivianite precipitation at most sites would not be possible.

In addition, vivianite formation may be hindered kinetically in sediments; i.e., vivianite precipitation does not occur and porewater remains supersaturated with respect to vivianite (Postma 1981; Nembrini et al. 1982). Thus, vivianite precipitation in porewater from our study lakes is unlikely.

Under aerobic conditions and with molar ratios of Fe to P greater than 1.8, iron oxy-hydroxides adsorb all soluble P; at ratios less than 1.8, some sorption may also occur (Tessenow 1974). Oxygen penetration into bottom sediments may be small (< 4mm; Carlton and Wetzel 1988); therefore porewater in the top 10 cm of the sediment was assumed to be anaerobic. Since little soluble ferric iron is present in anaerobic porewater, ferrous iron in porewater was likely the only form of iron

present in porewater. At 24 of the 28 sites in the study lakes, porewater Fe:P molar ratios were less than 1.8 (Table 7.2). Thus, when anaerobic porewater enters aerobic lakewater, insufficient iron was present to inhibit P release from porewater. However, a negative relationship between Fe:P molar ratio and [SRP] in lakewater just above the sediments suggest that some Fe-P sorption may occur (Chapter 3).

Precipitation of P and Ca in porewater as hydroxyapatite ($Ca_5(PO_4)_3OH$) was investigated with porewater concentrations of Ca, SRP and OH^- (Table 7.2). In the study lakes, IAP at all sites were greater than the equilibrium activity product; thus, precipitation of hydroxyapatite was possible (Table 7.2). However, IAP may be overestimated by 10^3 to 10^6 due to overestimates of phosphate (10 to 100 times) in the SRP analyses (as explained above). A correction of 10^6 for P concentrations would limit hydroxyapatite precipitation to 7 of 14 sites. In addition, formation of hydroxyapatite may be kinetically hindered (Stumm and Leckie 1970); porewater in many lakes was reported to be supersaturated with hydroxyapatite (Holdren and Armstrong 1986). Similar to vivianite, precipitation of hydroxyapatite may be unlikely.

Although the porewater P fraction is small and may limit P release from sediments (Bostrom et al. 1982), exchange between particulate fractions and porewater may sustain P release. Since exchange reactions take place in the order of minutes (Carritt and Goodgal 1954), P released from porewater could be replenished from exchangeable P fractions. In the study lakes, P contained in NaOH-P (the most labile exchangeable sediment P fraction) was, on average, 40 times greater than P in porewater (Table 7.3). Relationships between potential sediment P release by molecular diffusion and exchangeable P fractions (NaOH-P,

CDB-P) were significant; however, the relationships explained little of the variance (Chapter 3). In other studies, relationships between exchangeable P fractions and P desorption, algal growth and P release from sediments also indicate that a small porewater P fraction may not limit P release from sediments (Williams et al. 1980; Hosomi et al. 1981; Young and DePinto 1982; Messer et al. 1984; Drake and Heany 1987; Nurnberg 1988).

Thus, P release from shallow sediment in the study lakes is possible: in the study lakes, (1) gradients across the sediment-water interface exist, (2) P release is not prevented by sorption or precipitation reactions, and (3) P release is not limited by the relatively small P mass in porewater since it is supported by a large mass of exchangeable particulate P fractions.

Changes in lakewater P

During summer, changes in P mass in the epilimnion or trophogenic zone of deep (thermally stratified) lakes can be accounted for (in P budgets) by external P sources, P sedimentation, outflow of P and internal P release (from hypolimnion or shallow sediments). In 14 of 16 deep lakes, the mass of P calculated with short-term budgets was less than actually present in the trophogenic zone (Chapter 5). The discrepancy in P mass over the summer could not be explained by P transport from the hypolimnion to the trophogenic zone (Chapter 5). Thus, P release from shallow sediments was the only likely mechanism that could balance short-term P budgets; the average potential rate of shallow P release for 16 thermally stratified lakes was 2.2 $mg.m^{-2}.d^{-1}$ (range -3.8 to 11.3 $mg.m^{-2}.d^{-1}$; Chapter 5).

This potential release of P from shallow sediments was (1) similar

to aerobic P release rates determined with cores incubated under aerobic condition in the laboratory (range -2 to 83, mean 5 $mg.m^{-2}.d^{-1}$; Chapter 1), (2) less than rates determined from P budgets of shallow lakes in other studies (Table 7.4), and (3) similar to or greater than external P loading rates to the study lakes (Chapter 5). In addition, comparable summer P budgets were constructed for the epilimnetic zone of Shagawa and Mirror lakes (Lie 1977; Caraco et al. 1988); discrepancies were 1.5 to 18 $mg.m^{-2}.d^{-1}$, similar to the rates calculated in this study. The estimates of potential P release rates from shallow sediments are high compared to P loading from external sources. Thus, P release from shallow sediments into the trophogenic zone may be important for the P cycle in lakes during the summer.

Transport mechanism

Phosphorus release from shallow sediments was possible and likely occurred in the study lakes: (1) concentration gradients of P were present across the sediment-water interface and (2) trophogenic summer P budgets could not be balanced without P release from shallow sediments. To determine the likely mechanism of P release from porewater to lakewater, P release by molecular diffusion and groundwater flow was calculated (Chapter 5 and 6), and compared to discrepancies in short-term P budgets.

The average rate of P release by molecular diffusion was 0.24 $mg.m^{-2}.d^{-1}$ and P transport by groundwater was 0.43 $mg.m^{-2}.d^{-1}$ in six study lakes, where both rates were determined (Chapter 6; Table 7.5). Only one previous study provided a comparable estimate of advective P transport. At Lake Mendota, groundwater P transport was estimated as 0.31 $mg.m^{-2}.d^{-1}$ (Brock et al. 1982); this rate was similar to the

average estimate for six lakes in this study (0.43 $mg.m^{-2}.d^{-1}$). On average, P transport into the trophogenic zone by molecular diffusion from shallow sediments, by groundwater inseepage and by diffusion across the thermocline was 13, 5 and 1 % of potential release estimated from summer trophogenic P budgets (Table 7.4). Total transport by these three mechanisms accounted for 20 % of P missing in the trophogenic zone; thus, other mechanisms for P transport could be important.

In laboratory studies, P release by bioturbation was much faster than by molecular diffusion in the presence of Chironomus, Yoldia, Clymenella, or Pontoporeia (Aller 1978; Gallepp et al. 1978; Gallepp 1979; Quigley and Robbins 1986). However, P release in cores with tubificids, Pontoporeia, and pisiid clams was less than from cores without animals (Davis et al. 1975; Quigley and Robbins 1986). Since quantitative adsorption of P onto ferric iron was unlikely in aerobic porewater near the sediment-water interface of the study lakes, bioturbation should not decrease, but increase P release from shallow sediments. Van Eck and Smits (1986) used a diffusion coefficient for bioturbation and mixing 10 times greater than molecular diffusion coefficient. However, sediment P release was correlated to the abundance of some benthic organisms (Gallepp 1979; Quigley and Robbins 1986). Thus, the diffusion coefficient for bioturbation may depend on the benthic community (size and composition) present in the sediment. To estimate P release by bioturbation accurately, much more information is needed on the interactions between sediment characteristics and the benthic community.

Implications of P release from shallow sediments to lake management

In this study, I have established that P release from shallow sediments in the study lakes (1) likely occurs (Chapters 2,3,5,6), (2) is substantial (compared to other P sources; Chapters 5,6), and (3) takes place through several different transport mechanisms (Chapters 2,5,6). To my knowledge, this is the first study which integrates two different approaches (lakewater P budgets and sediment P analyses) to determine potential P release from shallow sediments.

Because the potential for P release from shallow sediments is large, its impact on lakewater in the trophogenic zone could be important. In the study lakes, rates of P release by molecular diffusion were correlated to exchangeable particulate P fractions (Chapter 3). In deep thermally stratified lakes, P release rates (estimated with summer P budgets) were greater in more eutrophic lakes with a greater extent of shallow sediments than in less eutrophic lakes with a smaller extent of shallow sediment (Chapter 5). In addition, the trophic status of nine deep and shallow lakes were correlated to characteristics of shallow sediments (e.g., mobile porewater P; Chapter 4). Although some studies hypothesized the significance of shallow sediments in P cycling in lakes (Hayes et al. 1952; Fee 1979), I found direct relationships between P in shallow bottom sediments and in lakewater for several lakes.

This interaction between P in shallow sediments and in lakewater is important in understanding P cycling in lakewater. The effect of restoration schemes (e.g., sewage diversion) on lakewater quality is usually evaluated with P loading models (e.g., Vollenweider 1968; Nurnberg 1984). When some P inputs are excluded from the loading models

(e.g., P release from shallow sediments), actual lakewater P concentrations will be higher than predicted from the model. In lakes where P release from shallow sediments is substantial (i.e., eutrophic lakes with a large extent of shallow sediments with high porewater P concentrations and high NaOH-P content; Chapter 3,4,5), the discrepancy in actual and predicted P concentrations would be greatest. Therefore, predicted improvements in lakewater quality due to implementation of lake "restoration" techniques may not be observed if P release from shallow sediments is ignored. In order to improve lakewater quality with lake management techniques, the potential importance of P release from shallow sediments should be recognized and taken into account.

7.1 REFERENCES

Aller, R. C. 1978. Experimental studies of changes produced by deposit feeders on porewater, sediment, and overlying water chemistry. Am. J. Sci. 278:1185-1234.

Bannerman, R. T., D. E. Armstrong, G. C. Holdren, and R. F. Harris. 1974. Phosphorus mobility in Lake Ontario sediments. p. 158-178. In Proc. 17th Conf. Great Lakes Research, Ann Arbor, MI.

Belanger, T. V., and D. F. Mikutel. 1985. On the use of seepage meters to estimate groundwater nutrient loading to lakes. Water Resour. Bull. 21:265-272.

Bengtsson, L. 1975. Phosphorus release from a highly eutrophic lake sediment. Verh. Internat. Verein. Limnol. 19:1107-1116.

Bostrom, B. 1984. Potential mobility of phosphorus in different types of lake sediment. Int. Revue ges. Hydrobiol. 69:457-474.

Bostrom, B., I. Ahlgren, and R. Bell. 1985. Internal nutrient loading in a eutrophic lake, reflected in seasonal variations of some sediment parameters. Verh. Internat. Verein. Limnol. 22:3335-3339.

Bostrom, B., M. Jansson, and C. Forsberg. 1982. Phosphorus release from lake sediments. Arch. Hydrobiol. 18:5-59.

Brock, T. D., D. R. Lee, D. Jones, and D. Winek. 1982. Groundwater as a nutrient source to a drainage lake; Lake Mendota, Wisconsin. Water Res. 16:1255-1263.

Caraco, N. F., J. J. Cole, G. E. Likens, M. D. Mattson, and S. Nolan. 1988. A very imbalanced nutrient budget for Mirror Lake, New Hampshire, U.S.A. Verh. Internat. Verein. Limnol. 23:170-175.

Carignan, R. 1984. Sediment geochemistry in a eutrophic lake colonized

by the sugmersed macrophyte Myriophyllum spicatum. Verh. Internat. Verein. Limnol. 22:355-370.

Carignan, R., and R. J. Flett. 1981. Postdepositional mobility of phosphorus in lake sediments. Limnol. Oceanogr. 26:361-366.

Carlton, R. G., and R. G. Wetzel. 1988. Phosphorus flux from lake sediments: effect of epipelic algal oxygen production. Limnol. Oceanogr. 33:562-570.

Carritt, D. E., and S. Goodgal. 1954. Sorption reactions and some ecological implications. Deep-Sea Res. 4:224-243.

Davis, R. B., D. L. Thurlow, and F. E. Brewster. 1975. Effects of burrowing tubificid worms on the exchange of phosphorus between lake sediments and overlying water. Verh. Internat. Verein. Limnol. 19:382-394.

Drake, J. C., and S. I. Heany. 1987. Occurrence of phosphorus and its potential remobilization in the littoral sediments of a productive English lake. Freshwater Biol. 17:513-523.

Fee, E. J. 1979. A relation between lake morphometry and primary productivity and its use in interpreting whole-lake eutrophication experiments. Limnol. Oceanogr. 24:401-416.

Frink, C. R. 1969. Chemical and mineralogical characteristics of eutrophic lake sediments. Soil Sci. Soc. Amer. Proc. 33:369-372.

Gallepp, G. W. 1979. Chironomid influence on phosphorus release in sediment-water microcosms. Ecology 60:547-556.

Gallepp, G. W., J. F. Kitchell, and S. M. Bartell. 1978. Phosphorus release from lake sediments as affected by chironomids. Verh. Internat. Verein. Limnol. 20:458-465.

Gjessing, E. T. 1964. Ferrous iron in water. Limnol. Oceanogr. 3:272-

274.

Hayes, F. R., J. A. McCarter, M. L. Cameron, and D. A. Livingstone. 1952. On the kinetics of phosphorus exchange in lakes. J. Ecol. 40:202-216.

Holdren, G. C., and D. E. Armstrong. 1986. Interstitial ion concentrations as an indicator of phosphorus release and mineral formation in sediments. p. 133-147. In P. G. Sly (ed.). Sediments and Water Interactions (Proc. 3rd Int. Symp. on Interactions between sediment and water; Geneva, Switzerland, Aug. 27-31, 1984). Springer-Verlag, New York, NY. 521p.

Hosomi, M., M. Okada, and R. Sudo. 1981. Release of phosphorus from sediments. Verh. Internat. Verein. Limnol. 21:628-633.

Jacoby, J. M., D. D. Lynch, E. B. Welch, and M. A. Perkins. 1982. Internal phosphorus release in a shallow eutrophic lake. Water Res. 16:911-919.

Kamp-Nielsen, L. 1975. A kinetic approach to the aerobic sediment-water exchange of phosphorus in Lake Esrom. Ecol. Model. 1:153-160.

Lean, D. R. S. 1973. Movement of phosphorus between its biological important forms in lakewater. J. Fish. res. Board Can. 30:1525-1536.

Lie, G. B. 1977. Phosphorus cycling by freshwater macrophytes - the case of Shagawa Lake. Ph.D. thesis, University of Minnesota-Minneapolis, Minneapolis, MN. 63p.

McKnight, D. M., B. A. Kimball, and K. E. Bencala. 1988. Iron photoreduction and oxidation in an acidic mountain stream. Science 240:637-640.

Messer, J. J., J. M. Ihnat, and D. L. Wegner. 1984. Phosphorus release

from the sediments of Flaming Gorge Reservoir, Wyoming, U.S.A. Verh. Internat. Verein. Limnol. 22:1457-1264.

Nembrini, G., J. A. Capobianco, J. Garcia, and J.-M. Jaquet. 1982. Interaction between interstitial water and sediment in two cores of Lac Leman, Switzerland. Hydrobiologia 92:363-375.

Nriagu, J. O., and C. I. Dell. 1974. Diagenetic formation of iron phosphates in recent lake sediments. Am. Mineral. 59:934-946.

Nurnberg, G. K. 1984. The prediction of internal phosphorus load in lakes with anoxic hypolimnia. Limnol. Oceanogr. 29:111-124.

Nurnberg, G. K. 1988. Prediction of phosphorus release rates from total and reductant-soluble phosphorus in anoxic lake sediments. Can. J. Fish. Aquat. Sci. 45:453-462.

Phillips, G. L. 1977. The mineral nutrient levels in three Norfolk broads differing in trophic status, and an annual mineral content budget for one of them. J. Ecol. 65:447-474.

Postma, D. 1981. Formation of siderite and vivianite and the porewater composition of a recent bog sediment in Denmark. Chem. Geol. 31:225-244.

Quigley, M. A., and J. A. Robbins. 1986. Phosphorus release processes in nearshore southern Lake Michigan. Can. J. Fish. Aquat. Sci. 43:1201-1207.

Rigler, F. 1966. Radiobiological analysis of inorganic phosphorus in lakewater. Verh. Internat. Verein. Limnol. 16:465-470.

Ryding, S. O., and C. Forsberg. 1977. Sediments as a nutrient source in shallow polluted lakes. p. 227-234. In H. L. Golterman (ed.). Interactions between sediments and freshwater (Proc. S.I.L.-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands.

Stainton, M. P. 1980. Errors in molybdenum blue methods for determining orthophosphate in freshwater. Can. J. Fish. Aquat. Sci. 37:472-478.

Stauffer, R. E. 1987. Vertical nutrient transport and its effect on epilimnetic phosphorus in four calcareous lakes. Hydrobiologia 154:87-102.

Stauffer, R. E., and D. E. Armstrong. 1984. Lake mixing and its relationship to epilimnetic phosphorus in Shagawa Lake, Minnesota. Can. J. Fish. Aquat. Sci. 41:57-69.

Stevens, R. J., and C. E. Gibson. 1977. Sediment release of phosphorus in Lough Neagh, Northern Ireland. p. 343-347. In H. L. Golterman (ed.). Interactions between sediments and freshwater (Proc. S.I.L.-Unesco Conf.). Junk and Pudoc, The Hague, the Netherlands.

Stumm, W. and J. O. Leckie. 1970. Phosphate exchange with sediments: its role in the productivity of surface waters. Proc. Int. Water Pollution Res. Conf. 5: San Francisco and Hawaii 3: Art 26. 16p.

Stumm, W., and J. J. Morgan. 1981. Aquatic chemistry. 2nd ed. Wiley-Interscience, New York, NY. 780p.

Tessenow, U. 1974. Losungs-, Diffusions- und Sorptionsprozesse in der Oberschicht von Seesedimenten. IV Reaktionsmechanismen und Gleichgewichte im System Eisen-Mangan-Phosphat im Hinblick auf die Vivianitakkumulation im Ursee. Arch. Hydrobiol. Suppl. 47:1-79.

Tiren, T., and K. Pettersson. 1985. The influence of nitrate on the phosphorus flux to and from oxygen depleted lake sediments. Hydrobiologia 120:207-223.

Van Eck, G. Th. M., and J. G. C. Smits. 1986. Calculation of nutrient fluxes across the sediment-water interface in shallow lakes. p. 289-301. In P. G. Sly (ed.). Sediments and Water Interactions

(Proc. 3rd Int. Symp. on Interactions between sediment and water; Geneva, Switzerland, Aug. 27-31, 1984). Springer-Verlag, New York, NY. 521p.

Vollenweider, R. A. 1968. Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular refence to nitrogen and phosphorus as factors in eutrophication. OECD Report DAS/CSI/68-27, Directorate for Scientific Affairs, Paris.

Wetzel, R. G. 1983. Limnology. 2nd ed. Saunders, Philadelphia, PA. 767p.

Williams, J. D. H., H. Shear, and R. L. Thomas. 1980. Availability to Scenedesmus quadricauda of different forms of phosphorus in sedimentary materials from the Great Lakes. Limnol. Oceanogr. 25:1-11.

Young, T. C., and J. V. DePinto. 1982. Algal availability of particulate phosphorus from diffuse and point sources in the lower Great Lakes basin. Hydrobiologia 91:111-119.

Table 7.1. Soluble reactive phosphorus (SRP) gradients across the sediment-water interface of shallow sediments, reported in or calculated from the literature and determined in this study.

Reference	SRP gradient (in $mg.m^{-4}$)
Bannerman et al. 1974	200 - 24,200
Carignan and Flett 1981	6250
Carignan 1984	0 - 10,500
Quigley and Robbins 1986	263
Van Eck and Smits 1986	28,000
This study	400 - 40,600

Table 7.2. Concentrations of soluble reactive phosphorus (SRP, in $mg.m^{-3}$), ferrous iron (Fe, in $mg.m^{-3}$) and calcium (Ca, in $g.m^{-3}$), and pH in porewater from the top 10 cm of the sediment collected from the depths (m) indicated in nine study lakes. Molar ratios of Fe to SRP and $Fe(OH)^{+}$ to Fe^{2+} (Fe^{*}) are indicated; $Fe(OH)^{+}$:Fe^{2+} was calculated with pH and equilibrium constant (K) 3.2×10^{-10} (Stumm and Morgan 1981). Ion activity products (IAP) are calculated for vivianite (uncorrected and corrected for $Fe(OH)^{+}$; $K = 5.0 \times 10^{-12}$) and hydroxyapatite ($K = 1.6 \times 10^{-58}$).

Lake	Depth	SRP	Fe	Ca	pH	Fe:SRP	Fe^{*}	IAP		
								vivianite		hydroxyapatite
								uncorr	corr	
Baptiste	2.5	518	334	33	7.9	0.4	0.03	7.8×10^{-11}	7.2×10^{-11}	4.6×10^{-51}
	4	347	224	32	7.8	0.4	0.02	6.3×10^{-12}	5.9×10^{-12}	4.3×10^{-52}
	5	397	182	35	7.9	0.3	0.03	7.5×10^{-12}	6.9×10^{-12}	2.8×10^{-51}
Figure 8	2.5	1955	629	-	7.8	0.2	0.02	4.4×10^{-9}	4.1×10^{-9}	
	5	3622	1010	-	7.8	0.2	0.02	6.3×10^{-8}	5.9×10^{-8}	
Island	2.5	132	251	24	8.1	1.1	0.04	6.0×10^{-12}	5.3×10^{-12}	1.1×10^{-52}
	4	528	251	25	8.2	0.3	0.06	1.6×10^{-10}	1.3×10^{-11}	2.4×10^{-50}
	5	261	212	25	7.9	0.5	0.03	5.1×10^{-12}	4.7×10^{-12}	1.5×10^{-52}
	7.5	206	214	30	7.9	0.6	0.03	3.3×10^{-12}	3.0×10^{-12}	1.8×10^{-52}
Jenkins	4	2274	399	-	8.0	0.1	0.03	4.0×10^{-9}	3.9×10^{-9}	
	5	1961	358	-	7.9	0.1	0.03	1.4×10^{-9}	1.3×10^{-10}	
	7.5	1857	339	-	8.1	0.1				
Long	2.5	342	1954	40	7.5	3.4	0.01	7.6×10^{-10}	7.3×10^{-10}	5.1×10^{-53}
	4	129	280	34	8.4	1.2	0.09	3.5×10^{-11}	2.7×10^{-11}	1.1×10^{-50}
	5	274	600	29	8.5	1.2	0.11	2.5×10^{-9}	1.8×10^{-9}	1.2×10^{-49}
Minnie	5	1573	1259	-	9.4	0.4	0.86	5.1×10^{-5}	7.8×10^{-6}	
	7.5	445	695	-	9.6	0.9	1.37	1.7×10^{-6}	1.3×10^{-7}	

Table 7.2. Continued

Narrow	2.5	124	211	34	7.7	0.9	0.02	3.9×10^{-13}	3.7×10^{-13}	9.0×10^{-54}
	5	29	119	35	7.8	2.3	0.02	6.6×10^{-15}	6.2×10^{-15}	3.9×10^{-55}
	7.5	35	65	26	7.8	1.0	0.02	1.6×10^{-15}	1.5×10^{-15}	1.6×10^{-55}
	10	86	603	33	7.8	3.9	0.02	7.5×10^{-12}	7.0×10^{-12}	7.6×10^{-54}
S-9	1	38	671	-	7.7	9.8	0.02	1.2×10^{-12}	1.1×10^{-12}	
	0.5	171	955	-	7.8	3.1	0.02	1.2×10^{-10}	1.1×10^{-10}	
	1	309	605	-	7.7	1.1	0.02	5.7×10^{-11}	5.4×10^{-11}	
	3	1143	575	-	7.8	0.3	0.02	1.2×10^{-9}	1.1×10^{-9}	
Tucker	2.5	665	222	-	8.9	0.2	0.27	4.9×10^{-9}	2.4×10^{-9}	
	4	231	137	-	9.0	0.3	0.34	2.2×10^{-10}	9.1×10^{-11}	
	5	332	109	-	9.0	0.2	0.34	2.3×10^{-10}	9.4×10^{-11}	
	7.5	287	205	-	9.0	0.4	0.34	1.1×10^{-9}	4.7×10^{-10}	

Table 7.3. The amount of phosphorus present as particulate NaOH-P and porewater SRP per 1 cm^3 at the nine study lakes.

Lake	NaOH-P	SRP	NaOH-P:SRP
	ug		
Baptiste	8.29	0.35	24
Figure Eight	14.4	3.84	4
Island	10.35	0.14	74
Jenkins	12.64	0.74	17
Long	4.64	0.26	18
Minnie	4.82	0.94	5
Narrow	5.33	0.04	133
S-9	9.42	0.17	55
Tucker	9.00	0.27	33

Table 7.4. Reported estimates of sediment phosphorus (P) release from P budgets of shallow lakes (i.e., lakes not thermally stratified during summer).

Reference	Sediment P Release (in $mg.m^{-2}.d^{-1}$)
Bengtsson 1975	-15 to 44
Phillips 1977	21.3
Ryding and Forsberg 1977	9 to 47
Stevens and Gibson 1977	14 to 38

Table 7.5. Estimates of P release from shallow sediments from trophogenic summer total phosphorus budgets (Budget), by molecular diffusion (Diff.), groundwater transport (Adv.) and transport from the hypolimnion (Hypo.); all rates are in mg $P.m^{-2}.d^{-1}$ (%) of Budget and are expressed over 1 m^2 of lake surface area.

Lake	Budget	Diff.		Adv.		Hypo.	
Baptiste	6.8	0.09	(1.3)	0.47	(6.9)	0.01	(0.1)
Island	2.5	0.13	(5.2)	0.16	(6.4)	0.05	(2.0)
Jenkins	-	0.52		1.58		-	
Long	1.7	0.35	(20.6)	0.12	(7.1)	0.01	(0.6)
Minnie	4.1	1.50	(36.6)	-		-	
Narrow	3.6	0.06	(1.7)	0.04	(1.1)	0.003	(0.1)
Tucker	-	0.30		0.21			
Average			(13.1)		(5.4)		(0.7)